CHEMISTRY

Editorial:
   The Most Remarkable Things
           Inside Front Cover

1956

$1.00

Twenty-ninth
Year

★ *A SCIENCE SERVICE PUBLICATION* ★

The Most Remarkable Things

"Organic chemistry nowadays almost drives one mad.
To me it appears like a primeval tropical forest, full of the
most remarkable things; a dreadful, endless jungle into
which one does not dare enter, for there seems to be no way
out."

The above words represent one viewpoint of the science of Organic Chemistry. But, strangely enough, these words were spoken over 100 years ago by the famous German chemist, Friedrich Wöhler!

The fact that organic chemistry is like a "primeval tropical forest" even more today is what makes the subject so fascinating and full of "the most remarkable things." How dull it would become if all the facts were known, if no further research were necessary, if the subject were completely and entirely understood! As it is, Nature presents to us a never-ending challenge which spurs us to probe ever deeper into her mysteries. For it seems that with each new discovery, new problems are presented and new roads are opened to hitherto unknown fields.

This book is certainly not intended as a treatise on the subject. Its primary purpose is to whet the appetite. It is hoped that enough interest will be kindled here to warrant more specialized study. For, never before has the need for trained personnel been so great! Never before have the opportunities been so tempting! Never before have the rewards been so large! With our knowledge of organic chemistry today, we have but scratched the surface. There is much that remains to be done, much that needs to be known, and many challenges that have to be met.

Our earnest hope is that you may find this subject so engrossing that you will want to pursue it further. And, if during this pursuit you help to clarify the complex, or to make known the unknown, or in some way help to better the understanding to the benefit of mankind, then our efforts will not have been in vain.

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Organic Reactions

▶ A MULTITUDE of articles used in our daily lives have been created through the science of organic chemistry. All of these articles are obtained by employing one or more basic chemical reactions. The common aspirin tablet, for example, is made by a process of *acetylation*. Materials such as nylon and synthetic rubber are made by using many complex reactions.

In order to acquaint you with just a few of these basic reactions, we will devote the first section to them. You will note that these reactions are used again in various ways for the preparation of the synthetic products described later on.

Oxidation

▶ FIRST, we will consider *oxidation*, a very important reaction used in the preparation of hundreds of compounds. Just what is oxidation? We usually think of it as a process which "adds oxygen" to a substance. But it involves much more than simply adding oxygen to a compound. Under the term "oxidation," we include the removal of hydrogen, or the replacement of a hydrogen atom by oxygen, or the breaking of a carbon-to-carbon linkage with the addition of oxygen, or even an increase in the valence of carbon.

The substance employed to perform one of the above operations is known as an *oxidizing agent*, and there are many of them used in organic reactions. Each one has certain advantages which make it suitable for a particular reaction. There are so-called "strong" oxidizing agents and "weak" oxidizing agents. In choosing an oxidizing agent for a particular reaction, the following must be kept in mind:

1. Is it strong enough to complete the desired reaction?

2. Will it form any undesirable side reactions?

3. Will it permit stopping the reaction at the desired point?

4. Will the compound formed as a result of reduction of the oxidizing agent interfere with the desired product?

You are familiar with the common oxidizing agents such as sodium dichromate and sulfuric acid, potassium permanganate, and nitric acid. Others used in organic reactions are nitrobenzene, lead peroxide, lead tetra-actetate, and, of course, the powerful ozone. It is also possible to oxidize by electrolytic reaction.

Oxidation of Primary Alcohols

Primary alcohols can be oxidized to form aldehydes first and then acids. If a "weak" oxidizing agent is used the corresponding aldehyde is obtained, but if a "strong" oxidizing agent is used the reaction continues to form the corresponding acid.

To prepare the oxidizing agent dissolve one gram of sodium dichromate in 10 cc. of water. (Although the sodium salt is preferable, you can use potassium dichromate if the former is not available.) Cautiously add one cc. of concentrated sulfuric acid and stir. Separate the solution into four equal portions in four test tubes.

Add 10 drops of ethyl alcohol to the first test tube. The alcohol is quickly oxidized to acetaldehyde, which you can recognize by its characteristic odor of green apples.

To the second portion of the oxidizing agent, add 10 drops of benzyl alcohol. This alcohol is oxidized to benzaldehyde which you will recognize from its odor of bitter almonds. If the reaction is slow, warm the solution *gently*.

To the third portion of the oxidizing agent, add 10 drops of iso-amyl alcohol. In this case iso-valeraldehyde is obtained, which has a pungent apple-like odor somewhat similar to that of acetaldehyde. Again, warm gently if necessary.

To the final portion of the oxidizing agent, add 10 drops of methyl alcohol. In this case you should obtain—formaldehyde? Well, only momentarily. You may notice a fleeting odor of formaldehyde, but methanol is so easily oxidized that the reaction tends to go all the way to formic acid and even further on to carbon dioxide and water. To obtain the aldehyde from methanol a different type of oxidation must be employed which we will consider later on.

In all the above oxidation reactions, you will note the yellow dichromate solution turns dark green. This is due to the reduction of the dichromate ion to the chromic ion. Using the ethyl alcohol as a typical reaction, we have:

$3C_2H_5OH + Na_2Cr_2O_7 + 4H_2SO_4$
$\rightarrow 3CH_3CHO + Cr_2(SO_4)_3 + Na_2SO_4 + 7H_2O.$
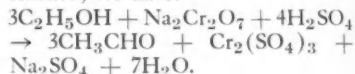
Oxidation of Aldehydes

Aldehydes are very easily oxidized to the corresponding acids. We could have continued our oxidation of the alcohols all the way to obtain the acids. However we shall use aldehydes as our starting point here in another illustration of the oxidation reaction.

Just for variety, suppose we use potassium permanganate this time for our oxidizing agent. Prepare a dilute solution of the reagent (about $\frac{1}{2}$ gram in 50 cc. of water) and pour a portion of it into three test tubes.

In the first tube, add 10 drops of acetaldehyde and stir. You should be able to recognize the vinegar-like odor of acetic acid. If not, warm the solution gently.

To the second portion add 10 drops of formaldehyde. Formic acid is obtained this time. Filter the solution and drop a piece of blue litmus paper in the filtrate. It should turn pink indicating the presence of formic acid.

To the third portion, add 10 drops of benzaldehyde. Benzoic acid is the end product of this reaction.

Dehydrogenation

Another phase of oxidation is known as *dehydrogenation*. A good example of this type of reaction is the formation of formaldehyde from methyl alcohol with metallic copper.

Wind one end of a clean copper wire into a small spiral. Grasping the other end with a pliers, heat the spiral in a flame until it glows bright red. Then plunge the red-hot wire into a solution of methyl alcohol diluted with a little water. Repeat this operation several times and you will soon be able to detect the presence of formaldehyde by its characteristic pungent odor.

No oxygen or oxidizing agent is employed in this reaction. Hydrogen is simply taken away. The copper is not an oxidizing agent, but a *catalyst*.

This method can only be used for the production of the more volatile aldehydes. Acetaldehyde can be obtained in this manner, although not quite as easily as formaldehyde. You may try it if you wish, proceeding exactly as for the methyl reaction.

So much for the oxidation of primary alcohols and aldehydes. The thing to remember is that primary alcohols are oxidized to aldehydes and aldehydes are oxidized to acids.

Now we should like to broaden our consideration of the oxidation reaction to include other types of compounds.

First, let us prepare the dichromate oxidizing agent which we shall use in several of the following reactions. Two grams of sodium (or potassium) dichromate are dissolved in 20 cc. of water. Cautiously add 4 cc. of concentrated sulfuric acid. Mix thoroughly and cool the solution.

Isopropyl Alcohol

What happens when a *secondary* alcohol is oxidized? In this case, the corresponding ketone is obtained, instead of an aldehyde. The oxidation of isopropyl alcohol to acetone will illustrate.

Pour about 3 cc. of the dichromate solution prepared above in a test tube and add 10 drops of isopropyl alcohol. Shake gently. After a short time, you should be able to recognize the mintlike odor of acetone.

Acetone

Acetone can be further oxidized to acetic acid, although not as readily as the alcohol. Using a fresh portion of the dichromate solution, add 10 drops of actetone. Shake and heat, but do not boil. Continue this procedure until the solution darkens and you can determine the odor of acetic acid. Carbon dioxide is also formed.

Glycerin

While we are on the subject, we must include the spectacular oxidation of glycerin. Glycerin is oxidized so rapidly that it bursts into flame. Place a few drops of glycerin in the center of a small metal dish. Cover completely with finely powdered potassium permanganate, and just wait. Soon the mixture will start to smoke and suddenly flare up with a bright bluish flame.

In aqueous solution, glycerin is oxidized to glyceraldehyde. Hydrogen peroxide is used as the oxidizing agent. Add a crystal of ferrous sulfate, and a few drops of glycerin. The glyceraldehyde upon further oxidation yields 3-hydroxy-2-oxopropanal, 2-oxopropanal, oxalic acid, formic acid, and carbon dioxide.

Oxalic Acid

To 3 cc. of water, add several drops of sulfuric acid and a few crystals of potassium permanganate. To this, add 10 drops of oxalic acid solution. The acid is oxidized to carbon dioxide and water and the permanganate is reduced to a colorless solution of manganese and potassium sulfates.

Ether

Ether is oxidized by chromic acid to form ethyl alcohol, acetic acid and ethyl acetate. Add a few drops of ether to 3 cc. of the dichromate solution in a test tube. Warm *gently* and shake occasionally. As the ether odor disappears, see if you can recognize the odor of one or more of the oxidation products listed above.

With alkaline potassium permanganate, the chief product obtained is potassium acetate. Proceed exactly as above, using a dilute solution of potassium permanganate made alkaline with sodium hydroxide solution instead of the chromate mixture.

Anthracene

When anthracene is oxidized, the product is *anthraquinone*, an important compound used in the manufacture of dyes. Place a small quantity of anthracene in a test tube with 5 cc. of glacial acetic acid and boil until the compound is entirely dissolved. Mix a small portion of the dichromate solution with an equal quantity of glacial acetic acid and add 10 drops to the anthracene solution. Crude anthraquinone separates out as a greenish-gray precipitate. Pure anthraquinone is a light yellow solid melting at 286° C.

Naphthalene

The oxidation product of naphthalene is *a-naphthoquinone*, which is a yellow solid. As with anthracene, the naphthalene is dissolved in boiling acetic acid and the chromate solution added. The *a*-naphthoquinone separates as a greenish precipitate.

Aniline

Aniline is very accommodating to the oxidation reaction. Depending upon the reagents used, the products obtained are nitrobenzene, nitrosobenzene, N-phenylhydroxylamine, benzoquinone, azoxybenzene and azobenzene, phenylquinonediimine, emeraldine, nigraniline, and various aniline blacks. We shall only attempt to obtain a few of these compounds. *Nitrobenzene* is formed with alkaline hypochlorite solution. Place a small quantity of calcium hypochlorite in a dilute solution of sodium carbonate. Stir thoroughly and add a few drops of aniline. Continue stirring until you can recognize the almond-like odor of nitrobenzene.

Along with other products, aniline black is obtained with chromate solution. You will readily recognize the deep black dye when a few drops of aniline are added to the chromate solution. Under controlled conditions, *quinone* can be obtained with the chromate solution. It can also be obtained by oxidizing the aniline with a solution of manganese dioxide in sulfuric acid. Potassium permanganate will oxidize aniline to yield azobenzene and nitrobenzene. In an alkaline medium, the azobenzene is obtained with ammonia. Hypochlorous acid will produce *p*-aminophenol.

Phenol

When phenol is oxidized, the benzene ring is broken and products

formed include oxalic acid, meso-tartaric acid, and carbon dioxide.

Dissolve a crystal of phenol in a little water which has been made alkaline with sodium hydroxide. Dilute potassium permanganate solution is then added.

Lactose

Lactose (milk sugar) is oxidized by nitric acid, yielding a mixture of mucic and oxalic acids.

Place one gram of lactose in an evaporating dish and add 5 cc. of concentrated nitric acid. Heat gently until the brown fumes appear. Then remove the flame, as the action will proceed of itself quite vigorously. After it quiets down a bit, again apply a gentle heat until the brown fumes are no longer evolved. (*Do not inhale these fumes!*) Add an equal volume of water to the remaining solution and allow to cool. If you care to obtain the products, evaporate the solution by half, allow to crystallize, and treat the crystals with warm alcohol. The oxalic acid will dissolve in the alcohol, and the remaining mucic acid can be recrystallized from boiling water.

Toluene

Toluene is oxidized to benzaldehyde and the latter to benzoic acid. Add finely powdered manganese dioxide to a dilute solution of sulfuric acid. To this, add 10 drops of toluene and shake. See if you can recognize the almond-like odor of benzaldehyde. Alkaline potassium permanganate will carry the oxidation further on to benzoic acid.

So much for oxidation. We have tried to include a wide variety of reactions which are typical of the oxidation procedure. Of course, we have but scratched the surface of this important aspect of organic chemistry, for many hundreds of oxidation reactions are performed constantly to obtain a multitude of useful compounds.

Nitration

➤ NITRATION is simply the process of attaching the nitro group (NO_2) to the carbon atom of a compound. And, we know you will be surprised to know, the substances performing this feat are called *nitrating agents*. The victims of the reaction become "nitro" compounds. Thus benzene is nitrated to form nitrobenzene, phenol to nitrophenol, toluene to nitrotoluene, etc. But, naturally, it is not quite as simple as this. According to the conditions present, many different compounds can be obtained. We have mononitro compounds, dinitro and trinitro (see under "nitrophenol" below). The nitro compounds are valuable links in the preparation of many vital organic substances. Polynitro compounds are used extensively as explosives.

The most logical substance to use for nitrating is nitric acid. However, for most reactions it cannot be used alone as it tends to act also as an oxidizing agent. It is usually mixed with sulfuric acid. The resulting liquid is commonly referred to as "mixed acids."

We are listing below four nitration

reactions which we hope will prove illustrative of the general process. We will consider benzene, phenol, naphthalene and cellulose. In the home laboratory our application of the nitration reaction must be limited. Some reactions are quite complex and others are highly explosive—not recommended for a home experiment.

Nitrobenzene

Place 3 cc. of concentrated nitric acid in a small flask. Add 5 drops of benzene and heat the mixture *gently* for a few minutes. Allow to cool and pour the mixture into a little water in a beaker. A heavy oily liquid separates out of the solution. This is nitrobenzene, sometimes called *oil of mirbane.* Note its odor of almonds, It is poisonous, do not inhale too strongly.

Nitrobenzene is used in the preparation of aniline. This reaction is a *reduction,* and we will discuss it later when we consider the reduction process.

Nitrophenol

Phenol is readily nitrated, yielding many products. Thus, we have the *mono*-nitrophenols (such as *o*-nitrophenol, *m*-nitrophenol, and *p*-nitrophenol), *di*-nitrophenols, and *tri*-nitrophenols. We will prepare a compound from the latter group—2,4,6-trinitro phenol, better known as *picric acid*. In this case the phenol must first be sulfonated and the resulting *p*-phenolsulfonic acid nitrated.

Heat on a *water bath* a mixture of 2 grams phenol with 2.5 cc. of concentrated sulfuric acid in a small flask for 20 minutes. Cool *thoroughly*, then add 7 cc. of concentrated nitric acid. A vigorous action results and large volumes of brown fumes will pour out of the flask. When the mixture calms down, heat again in a *water bath* for 30 minutes. Then add 20 cc. of water and immerse the flask in ice water. Picric acid separates out as a brilliant yellow precipitate. (*Caution*: *Picric acid explodes when rapidly heated or by percussion. Dispose of it immediately after experimenting by washing down the drain with water.*)

Nitronaphthalene

Although other compounds are known, we will only consider *l-nitronaphthalene* here. Place about $\frac{1}{2}$ gram of naphthalene in a dry test tube and add a solution of mixed acids (2 cc. of concentrated sulfuric acid and 1 cc. of concentrated nitric acid), keeping the mixture at a temperature of 50 degrees. The yellow l-nitronaphthalene forms as a layer on top of the solution.

Nitrocellulose

The nitration of cellulose yields several very interesting compounds known as cellulose nitrates or, collectively, as "nitrocellulose." Using filter paper as our source of cellulose, let us prepare a sample. Cautiously mix together 4 cc. of concentrated sulfuric acid with 5 cc. of concentrated nitric acid in a beaker. Cool the solution and add several strips of good quality filter paper. Allow the paper to soak in the solution for ten minutes. Then wash thoroughly with warm water and allow to dry. The product is similar to guncotton. Ignite one end of a strip. It burns rapidly with a brilliant flash.

Guncotton is used in making smokeless powder since, when it explodes, it yields only hydrogen, nitro-

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gen, steam, carbon dioxide and carbon monoxide, and produces no smoke.

Other cellulose nitrates, containing less nitrogen, form the compound known as *pyroxylin*. This compound is used to make celluloid.

Thus we have given a few examples of typical nitration reactions. Other compounds can be treated in similar ways to produce nitro-products. Remember that many nitro compounds are unstable and there is always the danger of explosion. Use care when experimenting with nitration reactions.

Many of our powerful explosives are produced by the process of nitration. (That is, they *were* considered powerful explosives before the advent of the atom bomb.) When a mixture of nitric and sulfuric acids is mixed with glycerine, *nitroglycerine* is obtained. Actually this compound is an ester and should be properly called glyceryl nitrate. It explodes when heated to 180 degrees or when struck.

The nitration of toluene produces several nitrotoluenes, among them *trinitrotoluene*, or T.N.T. It only explodes when detonated or burned in large quantities, thus it may be handled fairly safely.

Reduction

> IN DISCUSSING the oxidation reaction, we stated that it consisted of "adding" oxygen to a compound. And in considering nitration, we found that this reaction consisted of "adding" the nitro group to a compound. Now we have *reduction*, which is the process of "adding" hydrogen to a compound. Consequently, the reaction is sometimes referred to as "hydrogenation." It also includes the replacement of an oxygen, halogen, or sulfur atom by hydrogen.

Reducing agents are those compounds which readily provide a source of hydrogen. Hydrochloric acid and metal (zinc, tin, or iron) are the most popular reducing agents. In organic chemistry, sodium metal, sodium amalgam, stannous chloride or titanous chloride with acid, hydriodic acid, and sodium sulfite are some of the others used. Molecular hydrogen itself may be used if a proper catalyst

is employed (such as platinum, palladium, nickel, or copper chromite).

Organic compounds do not seem to like being reduced as well as they do oxidized. We find that the process of reduction is more difficult to carry out in the laboratory. In most cases the presence of a specially prepared catalyst is necessary.

The classic example of a reduction process is that of nitrobenzene to aniline. Previously we described the nitration of benzene to obtain nitrobenzene. You may prepare nitrobenzene in this manner for use here. Place about 2 cc. of the nitrobenzene in a large test tube. Drop in several small pieces of tin and add 5 cc. of hydrochloric acid. Gently heat the tube and shake occasionally to keep the reaction going at a steady rate. If necessary, add more tin or acid. The liquid will gradually turn dark brown in color. This is crude aniline. In the

reaction, the oxygen in the nitro group (NO_2) of the nitrobenzene is replaced by hydrogen to form the amino group (NH_2); thus we have *amino*-benzene (aniline) instead of *nitro*-benzene.

Aniline is not the only product formed from the reduction of nitrobenzene. If zinc dust and acid are used in the presence of ammonium chloride, *phenylhydroxylamine* is obtained. If the reduction is carried out in alkaline solution, *hydrazobenzene* is obtained. If nitrobenzene is reduced by electrolysis, *nitrosobenzene* is obtained. Thus, our product depends upon the type of reducing agent used in a certain environment.

In our oxidation reactions, we prepared formaldehyde and acetaldehyde from the corresponding alcohols (methyl and ethyl). Now, if we take the aldehydes—can we reduce them to obtain the alcohols? Place a few cc. of each aldehyde in separate test tubes. Add several pieces of zinc to each followed by a small quantity of dilute HCl. Allow the hydrogen to bubble through the solution for a few moments, then heat each solution just to boiling. Allow to cool slightly, then heat again. Repeat this process several times, adding more zinc or acid if necessary. The reduction is very slow without a catalyst; however, you may be able to obtain a small quantity of the alcohol. Filter the formaldehyde solution. Add some salicylic acid to the filtrate along with about 5 drops of concentrated sulfuric acid. Heat gently and smell *very cautiously*. Do you recognize any odor of wintergreen indicating the presence of methyl alcohol?

Treat the acetaldehyde solution simi-larly, using sodium acetate instead of the salicylic acid. This time see if you can recognize the fruity banana-like odor of ethyl acetate. Don't be too disappointed if you do not obtain phenomenal results. Our main point here is to illustrate the difficulty of reduction as compared with the ease of oxidation. As stated before, a catalyst must be employed for best results. In this reaction, finely divided nickel is often used. The nickel is prepared by the careful reduction of nickel hydroxide with hydrogen. We do not recommend this procedure for the home lab at this time.

We list below some other samples of the reduction process:

Acetamide is reduced to ethylamine by treatment with metallic sodium and amyl alcohol.

Acetylene can be reduced with an acid solution of chromous chloride to form ethene.

Aluminum ethoxide, prepared by the interaction of aluminum metal with ethyl alcohol in the presence of mercuric chloride, is an excellent agent for reducing various aldehydes and ketones to the corresponding alcohols.

Benzene can be reduced directly with hydrogen using a nickel catalyst. The product is cyclohexane.

Carbon tetrachloride is reduced to chloroform by the action of finely divided iron and water in the presence of the inevitable catalyst.

Ethane is obtained by the reduction of ethyl ether. In this case the reducing agent is hydriodic acid and red phosphorus.

Glucose can be reduced with sodi-

um amalgam and water to form D-sorbitol. Upon further reduction, hexane is obtained.

With the aid of catalyst, heat and pressure, hydrogen will reduce methyl alcohol to methane.

* * *

So much for the reduction reaction. Although the quantity of these reactions that can be illustrated by home experiments is limited, we hope that we have given you some idea of the reduction procedure. At least, do not be like the high school girl who asked the chemistry teacher for a supply of reducing agents. The puzzled teacher asked her what she wanted to do with them.

"Why, I want to *reduce*, of course," she replied.

Halogenation

➤ HALOGENATION is the process of adding a halogen to an organic compound. Depending on the halogen used, the process can be a chlorination, bromination, iodination, or fluorination reaction.

The introduction of fluorine in organic compounds is a relatively new field which promises to reveal many interesting and useful compounds. One example is the widely used refrigerant, "freon", (dichlorodifluoromethane) which is made by the action of antimony trifluoride on carbon tetrachloride.

Iodine does not render itself so readily for hydrogenation as the other halogens. The most important iodine compound is *iodoform*, obtained by the iodination of acetone or alcohol.

Bromine is very similar to chlorine in its reactions with organic compounds. It is used more in the laboratory because of the convenience of its physical state. *Bromobenzene* is an important bromine compound made by the bromination of benzene.

Chlorine is by far the most popular halogenating agent. It is active, easily prepared, economical, and forms many useful compounds. Among the compounds obtained are carbon tetrachloride, chloroform, ethyl chloride, chloral, chlorobenzene, etc.

Right now we will concern ourselves with chlorination. Chlorination can be performed by a variety of methods. One method is by using chlorine itself. A good example of this method is the formation of chloral from ethyl alcohol.

First of all, remember that chlorine is quite poisonous and very irritating to the mucous membranes. Perform this experiment with adequate ventilation and avoid inhaling the gas.

Arrange an apparatus as shown in the accompanying diagram. Place 2 or 3 grams of manganese dioxide in flask A and pour 5 cc. of hydrochloric acid on top of it through the thistle tube. Place 5 cc. of *warm* ethyl alcohol in test tube B. Add a small piece or iron, such as a tack, to the alcohol. This acts as a catalyst, or *halogen carrier*. Heat the flask until a steady flow of chlorine is produced. Allow it to bubble through the alcohol for a few minutes. Then apply gentle heat to

the alcohol, gradually increasing until it just begins to boil. Continue to bubble the chlorine through the gently boiling alcohol for about 10 or 15 minutes. Do not allow the alcohol to boil too vigorously, or you will lose most of it by evaporation. Several compounds are formed during this reaction, with chloral as the final product. Commercially, the chloral is separated by distillation with sulfuric acid. It dissolves in water to form chloral hydrate which is used in medicine as a sedative and hypnotic. When chloral hydrate is heated with sodium hydroxide solution, chloroform is obtained. When either chloral or the hydrate is condensed with chlorobenzene, DDT is obtained.

The direct chlorination of carbon disulfide by the above method produces carbon tetrachloride. However, we do *not* recommend this reaction for the home laboratory.

Hydrogen chloride can also be used as a chlorinating agent. The halogenation of turpentine to form bornyl chloride ("pinene hydrochloride") is one example.*

Chlorination can also be carried out by using sodium hypochlorite as the agent. A good example of such a reaction is the halogenation of acetone to obtain chloroform. Add 5 grams of sodium hypochlorite (or bleaching powder) to 20 cc. of water in a flask, and stir thoroughly. Then add, in small portions, a mixture of 1 cc. of acetone with 3 cc. of water. Shake thoroughly after each addition. Now, again you can use the same apparatus set-up. Remove the thistle tube and

* This will be discussed in the experiment on "Artificial Camphor" (Page 65).

insert a one-hole stopper in the flask with only tube C attached. Heat gently. Chloroform will distil over and condense in tube B, which should be immersed in ice water.

Now we would like to consider some of the other halogens in reactions of bromination and iodination.
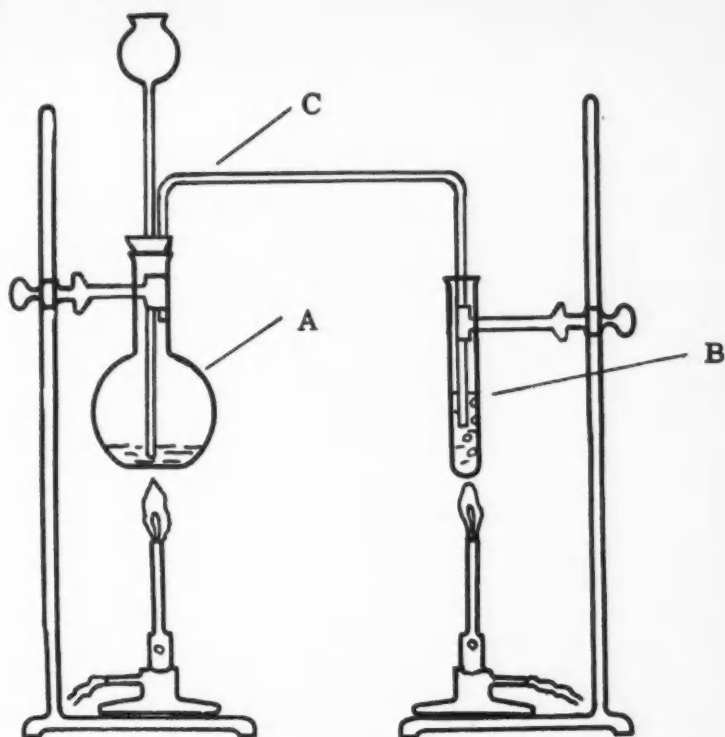
Reaction With Bromine

Bromine itself can be used for certain reactions. Usually it is advisable to use a compatible solvent. For example, in the bromination of acetanilid, acetic acid is employed as the solvent. We will use this as our demonstration reaction.

Bromine is rather unpleasant to handle. Not only is the vapor hazardous, but the liquid will cause severe burns if spilled on the skin. These burns are painful and extremely slow in healing. It is best to use rubber gloves and *adequate ventilation* when working with bromine. Although we do not recommend this experiment for the inexperienced, there should be no danger if common-sense safety precautions are heeded. If any bromine is accidentally spilled on the skin, remove the liquid as *rapidly as possible* by rinsing with large volumes of water. After this rub the area liberally with glycerin. After drying, apply an ointment or jelly such as is used in a heat burn.

Place in a small flask $7\frac{1}{2}$ cc. of glacial acetic acid and 5 cc. of water. Warm gently and add 3 grams of acetanilid. Stir until all of the solid is dissolved. Let the solution cool to room temperature. Now pour $2\frac{1}{2}$ cc. of glacial acetic acid in a test tube. Carefully add one cc. of bromine,

Basic apparatus for halogenation reactions

shake the tube *gently* and add to the acetanilid solution in the flask. Allow the flask to stand for about 15 minutes. The red color of the bromine will fade and some *p*-bromoacetanilid will crystallize. Add 75 cc. of water and stir. The *p*-bromoacetanilid will crystallize in quantity. If you care to collect the product, filter, wash with water, and recrystallize from hot water.

p-Bromoacetanilid, C_8H_8BrNO, is also known as "Antisepsin." It is insoluble in cold water, sparingly soluble in hot water. It has been used in medicine as an analgesic and antipyretic in the treatment of neuralgia and rheumatism.

With Bromine Water

Bromine water can also be used as a brominating agent. A good example of this reaction is the formation of tribromophenol.

Dissolve one or two crystals of phenol (carbolic acid) in 5 cc. of water in a small beaker. Add bromine water (an aqueous solution of bromine) until a *permanent* yellow color is obtained. Filter off the yellow precipitate and wash it thoroughly with a solution of sodium bisulfite. Follow this with clear water and finally dissolve the solid in about 10 cc. of hot alcohol. Filter the solution while hot and add about 25 cc. of hot water to the filtrate. Allow to stand. The 2,4, 6-tribromophenol will crystallize out of solution.

2,4,6-Tribromophenol, $C_6H_3Br_3O_3$, is very slightly soluble in water. It is used as an antiseptic and has also been used in medicine for the treatment of diarrhea and typhoid fever.

With Potassium Bromide

Potassium bromide can be used also as a bromination agent. In the production of ethyl bromide, which we shall describe, hydrogen bromide actually does the work of converting the alcohol to the bromide; however, potassium bromide is used as a source of bromine to produce the hydrogen bromide. In this reaction the hydroxyl group (OH) of the alcohol is replaced by bromine. Thus, instead of C_2H_5OH, we will have C_2H_5Br.

Place $3\frac{1}{2}$ cc. of ethyl alcohol in a 125-ml. Florence flask. Slowly add 4 cc. of concentrated sulfuric acid. Shake the mixture gently until the two liquids are thoroughly mixed. Now have ready a one-hole *cork* stopper to fit the flask. Insert a glass tube in the cork which leads to a flask partly filled with ice water. Allow the tube to dip just below the surface of the water. Now add 5 grams of granular potassium bromide to the acid-alcohol mixture and quickly insert the stopper and tubing arrangement. Heat the flask gently on a sand bath. The ethyl bromide will distil over and condense in the ice water in the receiving vessel. It will form oily drops on the bottom of the flask. You must regulate the temperature carefully during this distillation. If heated too strongly the solution is apt to foam excessively. On the other hand, you must apply sufficient heat to prevent the ice water from being sucked back into the reaction flask.

Ethyl bromide is a colorless, flammable liquid with an ether-like odor. The vapor is harmful, so do not inhale. It is used in organic synthesis and as a refrigerant.

Iodination

Iodine is not quite as cooperative in forming organic compounds as the other members of the family. The most popular iodine compound is *iodoform,* obtained by the iodination of alcohol or acetone.

Dissolve enough iodine crystals in potassium iodide solution to obtain a dark brown color. Add about 5 cc. of this solution to an equal quantity of alcohol. Next, add small portions of sodium hydroxide solution until the brown color disappears. Then heat the solution for a few minutes and allow to cool. Iodoform separates out as a yellow precipitate.

Iodoform, CHI_3, is a yellow compound wih a somewhat disagreeable "antiseptic" odor. It is only slightly

soluble in water. It is used chiefly as an antiseptic for wounds, chancroid, hemorrhoids, ulcers, and sundry skin diseases.

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Preparation of Bromine

If you do not have a supply of bromine, the small quantity required for the experiment can be easily prepared. In a large test tube place about one-half gram of manganese dioxide and an equal quantity of potassium bromide. Add 5 cc. of dilute sulfuric acid. Attach a *cork* stopper with delivery tube leading to another test tube immersed in a tumbler of ice water. Upon heating the first tube, deep brown vapors of bromine will be driven off and condense to liquid in the receiving tube. As bromine is difficult to store, it is best to prepare it when needed. Be sure to use adequate ventilation. If you do not, you'll sure wish you had! And don't forget to wear rubber gloves when working with bromine.

Sulfonation

➤ THUS FAR we have discussed the introduction of oxygen, nitrogen, hydrogen, and the halogens into organic compounds in reactions of oxidation, nitration, reduction and halogenation. Now we would like to consider the introduction of sulfur in a sulfonation reaction.

Sulfonation is the process by which the sulfonic acid group ($-SO_3H$) is attached to an organic compound, usually to the carbon or nitrogen atoms. Of course we immediately think of sulfuric acid as the logical sulfonating agent. And so it is, although in most cases it is very slow acting. For better results it is often necessary to intensify its action by increasing the SO_3 content (fuming sulfuric acid). Sometimes sulfur trioxide alone is used as the sulfonating agent. In other cases, chlorosulfonic acid is used.

Since neither fuming sulfuric acid nor chlorosulfonic acid are particularly recommended for use in a home laboratory, we shall use sulfuric acid alone even though it does take longer to accomplish its mission. We shall attempt to prepare sulfanilic acid by the sulfonation of aniline.

First, it is important that the aniline be freshly distilled. Distil about 10 cc. immediately before you begin the sulfonation reaction. Place the distilled aniline in a small Florence flask and carefully add, in small portions, 15 cc. of concentrated sulfuric acid. Shake after each addition. The reaction will be somewhat vigorous and it is best to cool the flask after each addition by immersing it in a container of cold water. The white lumps that separate out are aniline hydrogen sulfate.

The mixture must now be heated in an oil bath at 190 degrees for about four hours. The oil bath will enable you to control the temperature more evenly than otherwise. For this purpose ordinary vegetable shortening, such as "Crisco" or "Spry" will work very well. Place the shortening in a large beaker. Heat until it has all melted, then immerse the flask in the liquid fat (see diagram). Place a thermometer in the liquid in the flask and apply heat to the beaker until a
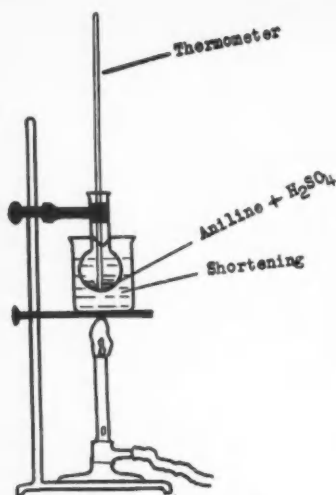
> SULFONATION *of Aniline*

temperature of 190 degrees is reached. Then regulate the heat so that this temperature is maintained as closely as possible.

After about four hours, you can test the solution to see if the reaction is completed. Place a few drops of the liquid in dilute sodium hydroxide solution. If, after stirring, the solid dissolves the product is ready. If a separation or precipitation of aniline is obtained, the mixture must be heated longer.

When the reaction is completed, as determined by the above test, pour the contents of the flask into a beaker containing approximately 100 cc. of cold water. Stir rapidly to avoid spattering. Crude sulfanilic acid is precipitated as a grey powder. Filter off the powder and wash it with cold water.

Purify the acid by dissolving the precipitate in the smallest amount of boiling water possible. Add about one gram of decolorizing charcoal (or bone black) and boil the solution for five minutes, stirring occasionally. Filter the solution quickly while still hot and set the filtrate aside to cool. As the solution cools, crystals of purified sulfanilic acid separate.

As you have probably deduced by now, sulfanilic acid is only sparingly soluble in cold water, much more so in hot water. It is soluble in sodium carbonate solution with the evolution of carbon dioxide. You can try this to test your product.

Sulfanilic acid is used in the preparation of certain indicators and dyes (such as Methyl Orange). The amide of sulfanilic acid is an important drug—perhaps you have heard of it—*sulfanilamide,* the first of the many "Wonder" drugs. If you care to keep your product, carefully dry the crystals, bottle, and label.

The sulfonation of benzene with sulfuric acid produces benzenesulfonic acid. Likewise, phenolsulfonic acid is obtained from phenol. In preparing picric acid we first used sulfonation on the phenol and then followed through with nitration. The first step in the production of sulfanilamide is the sulfonation of acetanilid with chlorosulfonic acid.

When we think of the remarkable properties of the sulfa drugs and the hundreds of lives saved through their administration, we can realize the importance of introducing sulfur into organic compounds!

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Hydrolysis

▶ THE WORD "hydrolysis" means decomposition by water. Therefore, we can define the reaction most simply by stating that "hydrolysis is the decomposition of organic substances by water". There are very few cases where water will do the job effectively alone and various accelerating agents such as acids, alkalies, or enzymes must be added. Thus these "accelerators" are known as hydrolyzing agents.

The meaning of the term hydrolysis has been extended to include various types of decompositions such as the inversion of sugars, breaking down proteins, and the saponification of fats. All of these reactions are possible with water alone, but they would be extremely slow and incomplete.

The best examples of hydrolysis for the home laboratory are the inversion of sugars and the saponification of fats. The former uses an acid as the hydrolyzing agent and the latter uses an alkali.

Ordinary cane sugar has the formula, $C_{12}H_{22}O_{11}$. Observe what happens when we treat it with water: $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

It has been broken down into two simpler substances by the action of water. In other words, it has been *hydrolyzed*. The two simpler sugars obtained are glucose and fructose.

Dissolve one gram of common cane sugar in 10 cc. of water in a test tube. Add about 20 drops of concentrated hydrochloric acid (acting as hydrolyzing agent). Heat the mixture

gently, but do not boil, for about 5 minutes. Allow to cool and then exactly neutralize the solution with dilute sodium hydroxide. To do this easily, add a few drops of phenolphthalein solution to the sugar solution. Add the alkali, drop by drop, until a *faint* pink color develops and does not disappear after shaking. You can then verify the presence of the simple sugars by adding Fehling's Solution and boiling the mixture for a minute or two. A reddish precipitate is obtained. When you add Fehling's Solution to an untreated solution of cane sugar, no such reaction is obtained.

Fehling's Solution consists of two solutions which are kept separate until ready for use. They are then mixed in equal volume and added to the solution to be tested. The solutions are prepared as follows:

Solution No. 1. Dissolve 1.5 grams of copper sulfate in 50 cc. of water.

Solution No. 2. Dissolve 8.5 grams of sodium potassium tartrate (Rochelle Salt) in 10 cc. of warm water. Add a solution of 2.5 grams sodium hydroxide in 10 cc. of water. Finally, dilute the mixture with 30 cc. of water.

Another reagent which will give the same test reaction as Fehling's solution is Benedict's solution. To make this reagent, dissolve 10 grams of sodium citrate and 6 grams of anhydrous sodium carbonate in 50 cc. of hot water. Add slowly, stirring constantly, a solution of 1 gram copper sulfate in 10 cc. water. Filter if the solution is not perfectly clear. Benedict's solution is used as is. No

mixing is necessary, and it will not deteriorate on standing.

Starch is also hydrolyzed to glucose. You can demonstrate by performing the same operation as above using suspended starch solution instead of the cane sugar.

Lactose, or milk sugar, has the same formula as cane sugar, $C_{12}H_{22}O_{11}$. It, too, can be hydrolyzed. The products are glucose and galactose.

Now let us consider the other phase of hydrolysis known as "saponification". Saponification usually consists of the hydrolyzing of oils and fats. By using acid as the hydrolyzing agent we obtain glycerin and the organic fatty acid. For example, the hydrolysis of crude coconut oil produces glycerin and coconut fatty acids which consist of a mixture of various acids such as lauric, myristic, palmitic, stearic, etc. However if the fats or oils are hydrolyzed with an alkali, the sodium salts of the fatty acids are obtained instead of the acids. These sodium salts are known more commonly as "soap". Both of these processes are widely used in industry. For another example, let us consider tallow. Tallow, a by-product of the meat and hide industries, is sold to the fatty acid producers and to the soapers. The fatty acid plants treat this tallow with acid and water to produce the mixture of fatty acids known commercially as "stearic acid" and oleic acid known commercially as "red oil", plus glycerin. Stearic acid is used in making candles, in shaving cream, cosmetics, etc. Red oil is used in the manufacture of plastics, driers, lubricating oils, etc.

The soap industry, on the other hand, treats the same tallow with alkali and water to produce soap plus glycerin. And, we assume, you already know what soap is used for.

Hydrolysis of fats with alkali is more easily accomplished in the home lab than with acid, so we will proceed with the manufacture of soap. Lard is more readily obtainable than tallow, so we shall use it for the fat. Place about 15 grams of lard in a small casserole. Dissolve 4 grams of sodium hydroxide in 15 cc. of water. Apply gentle heat to the casserole. When the lard is melted, add 5 cc. of sodium hydroxide solution to it, slowly and carefully, with constant stirring. Continue the heat with continual stirring for about 15 minutes. Then add the rest of the sodium hydroxide solution. Again, continue the heat, preferably on a steam bath, with occasional stirring, until the mixture hardens. Saponification is now complete and you have crude soap.

Esterfication

➤ IN ITS simplest form, we can define esterfication as the reaction between an acid and an alcohol. The result of this reaction is a compound known as an *ester*. For example, we can react a monohydroxy alcohol, such as ethyl, with an inorganic acid, such as nitric, to obtain the ester, *ethyl nitrate,* or with nitrous acid to obtain *ethyl nitrite*. By substituting a polyhydroxy alcohol, such as glycerol, we obtain glyceryl nitrate, an ester more

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commonly known as *nitroglycerine*.

Esters are formed with organic acids also. Examples: ethyl alcohol and acetic acid to obtain ethyl acetate; methyl alcohol plus formic acid to produce methyl formate; amyl alcohol with butyric acid to form amyl butyrate; butyl alcohol and stearic acid to obtain butyl stearate, and so on.

By far the most common ester is ethyl acetate, which is widely used as a solvent. It is also employed in the manufacture of smokeless powder, perfumes, artificial silks, films, and in artificial fruit essences.

The formation of ethyl acetate from alcohol and an acid represents a typical esterfication reaction which can be performed in the home laboratory. You will need a small distilling flask. If available, attach a condenser to the side arm of the flask. If not available, substitute a piece of glass tubing leading into a test tube which is immersed in a container of ice water. Carefully mix together 5 cc. of absolute ethyl alcohol with 6 cc. of concentrated sulfuric acid and pour the mixture into the distilling flask. Now insert a dropping funnel into the neck of the flask, making sure that the end extends *beneath* the surface of the liquid. (If you do not have a dropping funnel, use an ordinary funnel with a medicine dropper to add the liquid). Heat the flask in an oil bath. For details on an oil bath arrangement, see page 14. In another container mix together 7 cc. of glacial acetic acid with an equal volume of absolute ethyl alcohol. When the temperature of the oil in the oil bath reaches 145 degrees (test it by immersing a thermometer in the oil— not in the flask) the alcohol-acetic

acid mixture should be added *drop by drop*. As you add the mixture a reaction takes place and a portion of the liquid in the flask distills over. Continue to add the mixture, keeping the temperature of the oil at about 150 degrees. After all has been added, heat for another additional 5 or 10 minutes, then disconnect the apparatus.

To the distillate in the receiving vessel, add small portions of strong sodium carbonate solution until effervescence ceases. Allow the mixture to stand quietly for a while. Then carefully pour off the top layer. Add to it an equal volume of concentrated salt solution and shake thoroughly. Then add 5 cc. of ice water and shake again. Let stand until the liquids separate and draw off the upper layer. This is ethyl acetate.

For another example of esterfication, we can prepare butyl nitrite by the action of an inorganic acid with an alcohol. In a small flask, dissolve 3 grams of sodium nitrite in 44 cc. of cold water. Add exactly 3.6 cc. of n-butyl alcohol and stir thoroughly. Immerse the flask in a container containing ice and water. Insert a thermometer in the flask. When the temperature reaches 10 degrees, add in small portions a cold mixture of 3.8 cc. concentrated hydrochloric acid in the same volume of water. Shake and stir after each addition. Be sure to keep the temperature below 10 degrees during the entire reaction. After all is added, allow to stand in the cold solution for 15 minutes. The butyl nitrite will separate out.

Butyl nitrite is not an important compound and there is nothing spec-

tacular you can do with it. We include it here simply as a demonstration of an estertification reaction. However, do remember to handle it with care. *Do not inhale its vapors,* as they will cause severe headache.

In the section on synthetic perfumes and flavorings, we will prepare many other types of esters. As you will note, esters are responsible for a great number of pleasant-smelling preparations.

Acetylation

➤ THE PROCESS of acetylation consists of replacing the hydrogen atoms of certain organic compounds with the acetyl group. For example, when alcohol is acetylated with acetic anhydride, we obtain ethyl acetate. Ethyl alcohol is represented as C_2H_5OH. Replacing the hydrogen with the acetyl group (CH_3CO), we have $C_2H_5CH_3COO$, (ethyl acetate, more correctly written as $CH_3COOC_2H_5$).

One of the best known products of the reaction of acetylation is acetylsalicylic acid, or more commonly known as *aspirin*. Here the hydrogen of salicylic acid, $C_6H_4(OH)COOH$, is replaced by the acetyl group, CH_3CO, through acetylation, to produce the aspirin, $C_6H_4(OCOCH_3)$ COOH. The preparation of aspirin is one of the most convenient reactions to demonstrate the acetylation process in the home lab.

In a small flask carefully mix together 2 cc. each of acetic acid and acetic anhydride. Add 2 grams of salicylic acid and allow the mixture to boil gently for about ten minutes. Pour the hot solution into a beaker of cold water. Crude aspirin will separate out. To purify, filter off the crystals, carefully dry and recrystallize from hot water. Remember, this aspirin is not recommended for medical consumption! We suggest that you

still buy your aspirin tablets from the drug store!

When an amine, such as aniline, is subjected to acetylation, the product is acetanilide. The preparation of this substance is very similar to that of aspirin. Again, mix together equal quantities (about 5cc. of each) of acetic acid and acetic anhydride in a small flask. Carefully add 5cc. of *freshly distilled* aniline in small portions, shaking after each addition. (Remember, when distilling aniline to exercise caution as this compound is both flammable and poisonous.) Apply gentle heat to the mixture in the flask, allowing it to boil for about thirty minutes. Then pour the hot liquid into a beaker of water, stirring rapidly. Crude acetanilide separates out of solution.

The acetylation of cellulose produces an important product, *cellulose acetate,* which is used in the manufacture of rayon ("Celanese"). In a beaker stir together 10 cc. of glacial acetic acid with 3 cc. of acetic anhydride and add 2 drops of concentrated sulfuric acid, which acts as a catalyst in this reaction. Place a small tuft of absorbent cotton in this solution, pressing it well beneath the surface with a glass rod. Cover the beaker with a glass plate and let it stand quietly for about 24 hours or until the cotton is dissolved and a clear solu-

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tion is obtained. Pour this solution into a large container of water. Cellulose acetate is precipitated. In the manufacture of rayon, this substance is treated with acetone to form a viscous solution which in turn is forced through a spinneret. As the liquid comes into contact with air, the acetone evaporates and a filament of cellulose acetate remains.

The acetylation of glucose produces a product known as glucose penta-acetate. We know of no particular use for this product, but if you care to prepare it just for practice, proceed as follows: Grind thoroughly together in a mortar 2 grams of dry glucose with 1 gram of fused sodium acetate. Transfer the mixture to a flask and add 10 cc. of acetic anhydride. Heat,

with constant stirring, until all solids are dissolved. It will require some effort and about 30 minutes to obtain a clear solution. Then continue to heat for another two hours, preferably on a steam-bath. Pour the hot solution into a beaker of cold water, with stirring. The crude glucose penta-acetate will crystallize.

You have probably noted that practically the same procedure was used in the above reactions, that is, heating the compound to be acetylated with acetic anhydride. In many reactions, acetyl chloride is used as the acetylating agent instead of the anhydride. However, this product is not very pleasant to handle in the home lab as it has a very pungent odor and is extremely irritating to the eyes.

Diazotization

▶ IN 1858 the chemist J. P. Griess attempted to prepare 1,2-dihydroxy-4,6 dinitrobenzene by reacting picramic acid with nitrous acid. Instead he obtained a new compound hitherto unknown. He called the new compound *diazo,* because he assumed that it contained two nitrogen atoms in place of hydrogen in the benzene ring. What he had prepared was a diazo oxide compound which was not easily decomposed. By further experimenting he obtained other diazo compounds from various amines. Thus a new organic process was discovered from which many valuable compounds have been prepared.

This reaction, by which a diazo compound is obtained from a primary aromatic amine, is called *diazotization.* The diazonium salts are formed

by reaction with nitrous acid at low temperatures. Most diazonium compounds are not stable and usually are not separated from the aqueous solutions in which they are prepared. Dry diazonium compounds are explosive. Benzenediazonium chloride is a typical diazonium salt. In some ways this compound is similar to an inorganic salt, such as ammonium chloride. It ionizes in water with a chloride ion and the $C_6H_5N_2$ ion (positive). It reacts with silver oxide to form benzenediazonium hydroxide; however, potassium hydroxide converts it to potassium benzenediazotate.

The diazonium compounds are most useful in the roles they play for the synthesis of other important compounds. By replacement reactions and coupling reactions the diazonium

salts act as "intermediates", performing their important function and then leaving the scene.

In a beaker dissolve one gram of sodium carbonate in 25 cc. of water. Add 3 grams of sulfanilic acid and stir until the effervescence ceases. Then warm the solution until all solids are dissolved. Allow to cool, and add a solution of one gram of sodium nitrite dissolved in 5 cc. of water. Place the beaker in a mixture of crushed ice, salt and water. Stir the mixture with a thermometer until a temperature of 5 degrees is reached. At this time, add, drop by drop, a solution of 4 cc. concentrated hydrochloric acid in 8 cc. of water. Stir after each addition and do not allow the temperature to rise above 10 degrees. This completes the diazotization portion of our experiment. The compound obtained here in aqueous solution is benzenediazonium sulfonate. And we suggest you keep it in aqueous solution for, as pointed out above, these compounds have an annoying habit of exploding in the dry state. It is only sparingly soluble in water and will separate out as the hydrochloric acid is added. After all acid has been added, allow the solution to stand for two or three minutes

— no longer. Proceed immediately to the next step.

We now enter the "coupling" stage of our reaction. Mix together 2 cc. of dimethylaniline, 2 cc. of hydrochloric acid and 5 cc. of water. Cool, and add to the cold diazonium solution just prepared. Stir, and let stand for about 5 minutes. A deep red color should be formed. Next, add a solution of 3 grams sodium hydroxide dissolved in 10 cc. of water. Heat the mixture gently until a uniform orange color is obtained. Add 5 grams of salt and allow to cool. Filter and dissolve the precipitate in hot water. The coupling reaction with benzenediazonium sulfonate has produced p-dimethylaminoazobenzene-p sulfonic acid and the addition of sodium hydroxide has converted it to sodium p-dimethylaminoazobenzene-sulfonate.

To a portion of the orange solution add a little hydrochloric acid. Note a lovely red color appears. Now add sodium hydroxide. The solution turns yellow. Thus, this compound is useful as an indicator. It is more commonly known as *methyl orange*.

Another example of the diazotization reaction is described in the preparation of Aniline Yellow (see page 49).

Alcohols, Aldehydes, Acids

➤ Now that we have discussed some basic organic reactions, let us consider next three important groups of organic compounds: alcohols, aldehydes and acids. There are many, many types of alcohols such as the saturated monohydroxy group, the unsaturated monohydroxy group, the dihydroxy alcohols, trihydroxy, tetra, penta, hexa, etc., plus the aromatic alcohols (primary, secondary and tertiary). The discussion of all of these com-pounds is, of course, out of the scope of this book. So we have chosen three common alcohols: ethyl and methyl from the saturated monohydroxy group and benzyl, which is an aro-matic primary alcohol.

Each one of these three alcohols can be oxidized to form the corres-ponding aldehyde and the aldehyde, in turn, oxidized to form the corres-ponding acid.

The Methyl Series

➤ OF COURSE, you are familiar with the fact that carbon is an element with a valence of four, which means it has four bonds to which other elements can be attached. Now, if we bring in four hydrogen atoms and attach one to each bond of the carbon, we will have CH_4, which is *methane*, the parent of the methyl series. If we should remove one hy-drogen atom and replace instead with the hydroxyl group (OH), we have *methyl alcohol*, CH_3OH, which is considered below.

As demonstrated later, when meth-yl alcohol is oxidized formaldehyde is obtained: $2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$. Here, the hydrox-yl group has been replaced with an atom of oxygen. Since oxygen has two valence bonds, another atom of hydrogen must be displaced; thus the atom of oxygen is now attached to two bonds of carbon.

Further oxidation will produce for-mic acid, HCOOH. Here the hydro-xyl group is brought back, and a hydrogen atom has been removed.

Thus, like building blocks, the at-oms are rearranged to form new compounds.

Methyl Alcohol

➤ WE ARE ALL familiar with Methyl or "Wood" Alcohol, as it is a very useful substance. It usually is the chief ingredient of the non-permanent types of automobile anti-freeze. It is an excellent solvent which makes it

useful in the manufacture of paints, paint removers, artificial silk, photographic film, gums, resins, shellac, etc. It can serve as a fuel in place of ethyl alcohol. It is widely used as a denaturant for ethyl alcohol, rendering the latter unfit for drinking purposes.

Once upon a time wood alcohol was actually obtained from wood. When wood is distilled, it decomposes into charcoal and a volatile fraction which condenses to a liquor known generally as pyroligneous acid. Upon standing, this mixture separates into a heavy oil and a lighter aqueous fluid. This aqueous fluid contains the alcohol along with acetic acid, acetone and allyl alcohol. The methyl alcohol is separated by distillation.

But like so many of our organic reagents, methyl alcohol is now prepared synthetically. This is done by the combination of carbon monoxide with hydrogen at 350 degrees C. under pressure in the presence of a suitable catalyst, such as a mixture of copper, chromium and zinc oxides:

$$CO + 2H_2 \rightleftarrows CH_3OH.$$
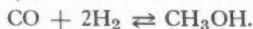
Primary alcohols are easily dehydrogenated by passing their vapors over metallic copper at 300 degrees. Although we casually speak of this as oxidation, actually no oxygen or oxidizing agent is involved; it is simply a process of eliminating hydrogen and is technically known as *dehydrogenation*.

In the home lab this can best be done by plunging a red-hot copper wire into the alcohol. Wind a thin copper wire around a glass rod several times to form a small coil, allowing about 6 inches of straight wire as a handle. Using a pliers, heat the coil to redness in the flame of an alcohol lamp or Bunsen burner. Plunge the hot wire into a small quantity of methyl alcohol in a test tube. Cool the test tube by immersing it in a beaker of cold water in order to prevent too much evaporation. Repeat this operation 5 or 6 times. Soon you will be able to recognize the pungent odor of formaldehyde.

If you do not wish to depend solely upon your nose, you may confirm the presence of formaldehyde by a chemical test. Dissolve a small quantity of alpha-naphthol in dilute sodium hydroxide solution. Add a few drops to the formaldehyde solution, and heat just to the boiling point. A light green color will form which will turn blue upon standing.

Oxidation to Formic Acid

Now if we proceed one step further with the "oxidation" we can obtain formic acid. In this case the reaction is actually an oxidation, as we are to use an oxidizing agent.

Dissolve 2 grams of potassium dichromate in 8 cc. of dilute sulphuric acid (use equal parts water and acid). Cool the mixture and add $\frac{1}{2}$ cc. of methyl alcohol dissolved in 4 cc. of water. Stir. The action may be vigorous and the solution turns dark green. Transfer to a flask and distill by applying gentle heat. If the reaction becomes too violent, remove the flame until it subsides. The colorless liquid obtained as the distillate is formic acid, as you can tell by its sharp, pungent odor. But, again, you can verify the presence of formic acid by a demonstration of its reducing action upon silver nitrate or mercuric chloride solutions. (See under "Formic Acid," page 24.)

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Do not forget that methyl alcohol is quite poisonous. When taken internally it causes intoxication, blindness, and finally, death. Even prolonged inhalation of its vapors can cause blindness. Therefore, use care in handling, and do not inhale the vapors more than is necessary. Do not allow it to spill on any open cuts or sores on the skin.

Formaldehyde

Formaldehyde is a colorless gas at ordinary temperatures. It is readily soluble in water and is usually sold in aqueous solution ("formalin") containing 37% formaldehyde. About the only practical way to prepare it is by the oxidation of methyl alcohol.

Wrap a clean thin piece of copper wire around a glass rod to form a tightly wound spiral. Grasp one end of the spiral with pliers and heat in the outer or oxidizing flame of a burner. When the wire glows bright red, plunge it into a solution of 1 cc. of methyl alcohol in 5 cc. of water. Remove the wire and quickly stopper the tube loosely. Shake gently. Reheat the wire and repeat the entire operation several times. Filter the solution. The filtrate should be a dilute solution of formaldehyde.

Like acetaldehyde, formaldehyde will reduce Tollen's reagent and Fehling's Solution. You can perform these reactions by referring to the section on "Acetaldehyde" substituting the formaldehyde solution just prepared for the acetaldehyde.

Formaldehyde reacts with ammonia to form a white solid known as hexamethylenetetramine. To 5 cc. of formaldehyde solution (37% variety) add 2 cc. of concentrated ammonium hydroxide and allow the mixed liquids to stand for a while. Then carefully evaporate to dryness. The hexamethylenetetramine remains. This compound, also known as methenamine, is used in vulcanizing rubber and in the manufacture of artificial resins.

To a dilute solution of formaldehyde (about 50% formalin with 50% water) add an equal volume of a dilute solution (about 10%) of sodium hydroxide. Heat the mixture gently to boiling for a few minutes. In this reaction simultaneous oxidation and reduction of the aldehyde occur with the formation of methyl alcohol and sodium formate. This change, which is characteristic of certain aldehydes, is known as the Cannizzaro Reaction. We will have occasion to use it again in other experiments.

When formaldehyde is evaporated to dryness, there is obtained a white amorphous solid which is *paraformaldehyde,* or "polymerized" formaldehyde. Formaldehyde forms many polymers. For another example, add a drop of concentrated sulfuric acid to 10 cc. of formaldehyde solution and evaporate almost to dryness.

Formaldehyde reacts with one of the protein constituents of milk to produce a violet coloration. This reaction was used as a test for formaldehyde in milk. Since the use of formaldehyde has been prohibited as a preservative of milk the test has little value today. If you would like to try it, add a drop of formaldehyde to a mixture of 5 cc. of milk in 5 cc.

of water. Add a few drops of 10% ferric chloride solution. Now incline the tube at an angle and very carefully pour 5 cc. of concentrated sulfuric acid down the side so that it forms a layer on the bottom and does not mix with the milk solution. A violet ring, forming at the junction of the two liquids, indicates the presence of formaldehyde. If the violet color does not form, heat the tube gently by immersing it in hot water.

Another test for formaldehyde can be made by using resorcinol. Prepare a 0.5 per cent solution of this compound and add a few drops of it to a dilute formaldehyde solution. Now pour this solution very carefully down the side of a second tube containing 5 cc. of concentrated sulfuric acid. Incline the second tube so that the liquids form two layers and do not mix. A reddish-violet coloration will appear where the two liquids meet.

Formaldehyde is used as a germicide and fungicide and in many industrial applications. One of the more important uses is in the manufacture of phenolic resins. The popular "Bakelite" is the best known of these resins and its preparation is described on page 60.

Formic Acid

Prologue

➤ WERE you ever stung by a bee? If so, you are familiar with one property of formic acid. It is said that the pain and swelling caused by the stinging of bees, hornets, and wasps is due to the injection of small amounts of formic acid.

Formic acid was first obtained in 1670 by S. Fisher as the result of the distillation of red ants. Whatever gave Mr. Fisher the idea of distilling ants we do not know, but anyway, this was the method by which formic acid was first prepared.

The Preparation

If you do not have a supply of red ants handy, don't fret—there are other methods you can use to prepare formic acid.

In our investigation of methyl alcohol, we demonstrated the preparation of formic acid by oxidizing the alcohol. However, formic acid can also be obtained from oxalic acid and glycerin as follows: Place 5 cc. of glycerin in a small flask and add 3 grams of oxalic acid. Fit the flask with a 2-hole stopper carrying a delivery tube extending to a receiving flask which is externally cooled. Insert a thermometer through the other hole in the stopper, allowing it to immerse in the glycerin. Heat the mixture *slowly* to 110° C., when formic acid will pass over and condense in the cool receiving flask. After a short time, allow the mixture to cool; then add more oxalic acid (about 2 grams) and heat again to 110°. Repeat the procedure until you obtain a sufficient quantity of formic acid. It is important that additional oxalic acid be added at frequent intervals.

Of the two methods outlined, we believe the above will give you a better yield of a more concentrated acid.

The Confirmation

Add a small quantity of sodium carbonate and potassium permangan-

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ate to the solution of formic acid and heat gently. Manganese dioxide is precipitated, which you will recognize as a deep brown coloration.

Add mercuric chloride solution to formic acid and warm. The mercuric chloride is reduced to mercurous chloride which appears as a white precipitate. Or, if your formic acid is concentrated, the reduction proceeds further and metallic mercury is obtained as a grey precipitate.

Place a few cc. of silver nitrate solution in a clean test tube and add 2 or 3 drops of dilute sodium hydroxide solution. A brown precipitate of silver oxide is formed. Now add dilute ammonium hydroxide, drop by drop, until the precipitate is *almost* redissolved; then add a few drops of formic acid. A silver mirror or a grey precipitate of metallic silver is obtained.

The Decomposition

Add 2 cc. of concentrated sulfuric acid to an equal quantity of formic acid in a test tube and heat gently. The acid is decomposed and carbon monoxide is given off:

$$HCOOH \rightarrow CO + H_2O$$
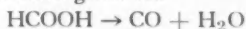
The sulfuric acid acts as a dehydrating agent in this case, simply removing a molecule of water to leave a molecule of carbon monoxide. You can ignite the gas as it is evolved; it burns with a blue flame.

If your formic acid is too dilute, carbon monoxide will not be formed. If this is the case, add sulfuric acid to dry sodium formate (see below) and heat gently. Of course, you know that carbon monoxide is highly poisonous; therefore, work with caution.

The Off-Spring

Sodium formate. The sodium salt is obtained by neutralizing formic acid with sodium hydroxide solution. There are several ways of doing this, but we prefer to color the NaOH pink with phenolphthalein and then add the acid, drop by drop, until the pink color *just* disappears. The solid sodium formate is obtained by evaporating the neutral liquid.

Lead Formate. Boil 5 cc. of formic acid with a little lead oxide-yellow (litharge, PbO) for several minutes; then filter rapidly and pour the filtrate into a watch glass. Lead formate will crystallize readily as the solution cools.

Copper formate. Repeat the above using copper oxide (CuO) in place of the lead oxide.

Epilogue

Commercially, formic acid is prepared by heating carbon monoxide with sodium hydroxide under pressure and then treating the resultant sodium formate with H_2SO_4. It is very caustic to the skin and concentrated solutions will produce painful burns. As illustrated in our confirming test, formic acid is a strong reducing agent. It is also a powerful antiseptic.

Now the next time you are stung by a bee, you will know all about the substance which irritates your skin and your disposition.

The Ethyl Series

➤ THE ETHYL series is very similar to the methyl group, except that the compounds are a little more complex. Here the parent substance is *ethane,* C_2H_6. Here we have two atoms of carbon in each molecule, attached to each other, with three atoms of hydrogen attached to the three remaining bonds of each atom. Again, replacing one hydrogen atom with the hydroxyl group, we obtain ethyl alcohol, C_2H_5OH. As in the methyl series, oxidation will produce an aldehyde and then an acid.

Ethyl Alcohol

➤ ETHYL alcohol has been produced for many years by a process of fermentation and distillation. We can demonstrate this procedure on a small scale in the home laboratory. But just remember to keep it on a small scale!

Yeast is composed of living cells, which produce bio-chemical substances known as *enzymes.* One of these enzymes, *zymase,* is responsible for the transformation of simple sugars (such as dextrose, glucose, levulose, etc.) into carbon dioxide and alcohol: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$. The more complex sugars, such as sucrose (cane sugar), maltose, etc., are first changed into the simple sugars by the enzyme, *invertase,* also produced by yeast: $C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$. The alcohol is then formed as before by the action of zymase. Therefore, a variety of sugars can be used to produce alcohol—cane sugar, molasses, corn syrup, dextrose, malt, etc.

Preparation

For home preparation, table syrup is perhaps the most convenient to use. Prepare 500 cc. of solution using one part syrup to three parts water. Crush a yeast cake in a small quantity of warm water making a thin paste, and pour into the syrup solution. Stir; let stand in a warm place for a few days, and Nature will do the rest.

After fermentation has taken place, pour off a portion of the liquid, being careful not to stir up the yeast sediment. Transfer to a distilling flask and distill the liquid at a temperature of about 85°. If you have a Liebig condenser, it can be very conveniently used for the distillation. If not, a glass tube leading to a container externally cooled will suffice. A thermometer should be inserted through the stopper of the distilling flask for temperature control.

Tests

Perhaps the simplest test is to determine whether your alcohol will burn. Apply a lighted match to a small quantity of the liquid in a watch glass. If the match is extinguished, it is obvious that the percentage of alcohol is not very high. In this case, it is advisable to redistill, being careful not to heat too strongly.

Next, you can perform the acetate test. Stir a few cc of the alcohol with an equal quantity of acetic acid (or a few crystals of sodium acetate). Add a small portion of sulfuric acid and

warm gently. You will soon recognize the fruity odor of ethyl acetate, sometimes referred to as "banana oil," (although banana oil is actually isoamyl acetate).

Uses

Industrially, alcohol is used in the manufacture of celluloid films, artificial leathers, varnishes, shellacs, and hundreds of other similar products.

Commercially, it is sold as fuel and is widely used as an anti-freeze, in burners, and as a solvent.

Medically, it is employed in the preparation of ethylene, chloroform, ether, iodoform, tinctures, and in numerous medicines. Externally as a rubbing compound and sterilizing agent. Internally, as a stimulant, narcotic and stomachic.

Socially, its use in wines and liquors is well known.

Morally, its use is frowned upon . . . "wine is a mocker, strong drink is raging: and whosoever is deceived thereby is not wise. . ."

Solid Alcohol

You no doubt have heard of "canned heat", which is usually a form of solid alcohol. It can be made from soap and alcohols, although more conveniently in the home lab by using calcium acetate. The alcohol should be of fairly high concentration (denatured alcohol can be used in this case). Prepare a saturated solution of calcium acetate and add to it a small quantity of alcohol. The solution will solidify into a jelly-like mass. Transfer a portion of the solid to a watch glass and ignite.

The Green Flame

Dissolve as much boric acid as possible in a small quantity of alcohol, heating if necessary. If the alcohol is now ignited, it will burn with a green flame.

Acetaldehyde

➤ ALTHOUGH we have prepared acetaldehyde by oxidation of ethyl alcohol, it is rather difficult to separate the product unless rather elaborate apparatus is used. Consequently, we will describe another method for preparing a small quantity in the home lab.

The method is by the destructive distillation of a mixture of calcium acetate and calcium formate. Mix thoroughly together in a mortar one gram of dry calcium acetate with one gram of calcium formate. Transfer the powders to a dry test tube. Clamp the tube in an inclined position on a ring stand and fit it with a one-hole stopper and delivery tube extending to another test tube which is immersed in ice water. Heat the mixture of powders gradually and evenly. Avoid overheating. The acetaldehyde will distil over and condense in the cooled receiving tube. Remember, acetaldehyde is highly flammable so exercise reasonable caution when working with it.

If calcium acetate or formate are not available, you can prepare your own. Simply add calcium carbonate to a hot solution of acetic or formic acid in water until no more dissolves. Then filter and evaporate the filtrate to dryness.

Acetaldehyde is colorless when pure and boils at the low temperature of

21 degrees. Because of the low boiling point, it is difficult to store acetaldehyde. It must be kept tightly stoppered in a cool place. It has a pungent odor and should not be inhaled too strongly as it irritates the mucous membranes.

Acetaldehyde will deposit silver from an ammoniacal silver nitrate solution (Tollen's reagent). In a *thoroughly clean* test tube place 2 cc. of a 5% solution of silver nitrate. Add one drop of 10% sodium hydroxide solution. Next add a 2% solution of ammonium hydroxide, drop by drop, until the precipitate *just* dissolves. Add a few drops of acetaldehyde immediately to this solution. Mix thoroughly and warm gently. If the test tube was thoroughly clean, a silver mirror will form on the walls. If not, a black precipitate of finely divided silver is obtained instead. The ammonia-silver nitrate solution described here should never be stored or strongly heated. Upon standing, a highly explosive precipitate is deposited. Therefore the reagent should always be prepared and used immediately.

Acetaldehyde will also reduce Fehling's Solution. Add a few drops of the aldehyde to Fehling's Solution (or Benedict's Solution. See page 15 for preparation details). Boil the solution for a few minutes. Note the precipitate formed.

To 1 cc. of pure acetaldehyde in a test tube, cautiously add *one* drop of concentrated sulfuric acid. Mix well. Note the tube grows quite hot. In this reaction, *paraldehyde* is obtained. The process by which it is formed is called *polymerization*. Further polymerization yields metaldehyde, aldol, and aldehyde resin.

To 1 cc. of a fairly concentrated solution of sodium hydroxide, add a drop or two of acetaldehyde and carefully boil for a few minutes. Note the solution is light yellow at first, changes to orange, and finally a red-brown liquid separates out. This is "aldehyde-resin" and it has a characteristic sweet, sickening odor.

Acetic Acid

➤ CERTAINLY acetic acid is the most familiar of all the organic acids. It is best known as the chief acid constituent of vinegar. When cooled to below 16 degrees, pure acetic acid forms colorless crystals. These crystals resemble ice in appearance; hence the pure acid is usually called "glacial" acetic acid.

There are many ways to prepare acetic acid. It can be obtained by the oxidation of ethyl alcohol which in turn is prepared by fermentation. Or, it can be obtained from cider vinegar which is prepared from the juice of apples. For a long time acetic acid was produced by the distillation of wood. Seven gallons of acid were extracted from one ton of wood. Acetic acid is also produced by synthetic methods. One such method employs acetylene as the starting point which itself is obtained as a by-product in the production of hydrogen during the refining of petroleum. The acetylene is passed through a dilute solution of sulfuric acid containing a catalyst. Acetaldehyde is formed by this

reaction and is then oxidized to acetic acid.

The most convenient way to prepare glacial acetic acid in the home lab is by the distillation of sodium acetate with sulfuric acid. Place 10 grams of sodium acetate in an evaporating dish. Apply *gentle* heat and continue heating, with stirring, until the water of crystallization is driven off and a dry powder remains. Be very careful not to heat too strongly, as the compound will decompose and char. Transfer the powder to a flask and add 7 cc. of concentrated sulfuric acid. If a condenser is available, fit it quickly to the flask. If not, substitute a one-hole stopper and glass tubing leading to another vessel immersed in ice water. Heat gently. Acetic acid distills over and collects in the receiving container. If you care to

purify the acid, it must be distilled again and that portion boiling at about 116 degrees should be collected.

To demonstrate how easily acetic acid freezes, immerse a partially filled test tube of the pure acid in a solution of ice, salt and water.

With inorganic compounds, acetic acid forms salts. For example, neutralization with sodium carbonate will produce sodium acetate. And, using calcium carbonate, calcium acetate is obtained. By heating dry calcium acetate, acetone is produced. Similarly, ammonia will produce ammonium acetate and from this compound *acetamide* is prepared.

With organic alcohols, acetic acid forms esters. These compounds are described in more detail elsewhere. (See pages 16 and 52).

The Benzyl Series

➤ Again, we find a similarity in the benzyl series to the ethyl and methyl group. But here the compounds are much more complex. The parent substance is benzene, C_6H_6. You will note that each molecule of benzene has six atoms of carbon and six atoms of hydrogen. As you can perhaps visualize, there is an opportunity here to produce many types of alcohols,

depending on where and how the hydroxyl group is attached. These alcohols are known as the "aromatic" alcohols, as compared to the "aliphatic" alcohols, such as methyl and ethyl.

As in the case of the aliphatic alcohols, benzyl alcohol is oxidized to an aldehyde and an acid.

Benzyl Alcohol

➤ We are all familiar with ordinary alcohol and wood alcohol, but how much do we know about the other alcohols? There are many other alcohols having interesting and useful properties with which we should become better acquainted.

Benzyl alcohol $C_6H_5CH_2OH$, is found free in Peru balsam and in combination in Tolu balsam, storax and cherry laurel. It is a clear, colorless liquid with a faint aromatic odor and a sharp burning taste. It differs from ordinary alcohol in that it is not very soluble in water.

Oxidation

Ethyl alcohol is oxidized to acetaldehyde and acetic acid. Methyl alcohol is oxidized to formaldehyde and formic acid. And, in a similar manner, benzyl alcohol is oxidized to benzaldehyde and benzoic acid.

Mix together 1 cc. of concentrated nitric acid with 4 cc. of water and add 5 drops of benzyl alcohol. Heat gently. You will soon be able to recognize the familiar bitter-almond odor of benzaldehyde.

To carry the oxidation further, continue to boil the mixture until the odor of benzaldehyde disappears. Be careful in heating this mixture, as it tends to boil in spurts and is liable to boil out of the tube. Always hold the test tube *away* from your face. When the almond odor can no longer be detected, discontinue heating and immerse the tube in a container of cold water. Benzoic acid will crystallize out.

Reaction With HCl

Mix 1 cc. of benzyl alcohol with 2 cc. of concentrated hydrochloric acid in a test tube and heat gently. Note the odor *cautiously*. This is benzyl chloride. It is a potent *lachrymator*, which means its vapors induce irritation in the nostrils, pain in the eyes, and a heavy flow of tears. This property is characteristic of many aromatic compounds containing a halogen in the side chain. They find use in chemical warfare agents and in "tear gas."

Reaction With H_2SO_4

Now when we treat ordinary alcohol with sulfuric acid we obtain an alkene (ethylene). Not so with benzyl alcohol. The action between sulfuric acid and benzyl alcohol forms a resin.

Place 1 cc. of benzyl alcohol in a large test tube and *carefully* add an equal quantity of concentrated sulfuric acid. Warm gently. Again, use care as the liquid may tend to spurt out of the tube. Do not heat strongly. Note that the solution gradually solidifies. Allow it to stand and it will harden into a plastic-like resin.

Benzyl alcohol and its esters are used in the manufacture of synthetic perfumes.

Benzyl acetate is present in the gardenia. You can prepare it by mixing together 1 cc. each of the benzyl alcohol and glacial acetic acid. Add just one drop of sulfuric acid and warm the mixture for a few minutes. Remove from the flame and smell cautiously. Note the pear-like odor. You will be able to detect the odor better if you allow the mixture to cool a bit.

Benzyl benzoate is present in Peru and Tolu balsams. It has a pleasant, although rather faint, odor. Add a small quantity of benzoic acid crystals to 1 cc. of benzyl alcohol in a test tube followed by one drop of sulfuric acid. Again, heat gently and note the odor.

Benzyl salicylate has a somewhat "minty" odor. It is prepared as outlined above using salicylic acid in place of benzoic acid.

Just to try something different, mix together the benzyl benzoate and salicylate just prepared and warm for a short time. Allow to cool. The resultant odor is somewhat difficult to describe and we shall let you be the judge as to whether it is good or bad.

By experimenting in this manner you can obtain some unusual fra-

grances — some pleasant and some otherwise. But whenever you try something new or unfamiliar to you, remember to exercise caution. Use only very small quantities and never sniff at a mixture that is boiling or reacting.

Benzyl alcohol also finds use in medicine as an antiseptic and in industry as a solvent for cellulose acetate.

It can be prepared by reducing benzaldehyde with sodium amalgam and water, by hydrolyzing benzyl chloride or by the action of potassium hydroxide on benzaldehyde. This latter method is known as the Cannizzaro reaction.

Benzaldehyde

► IN THE kernels of various fruits such as cherries, peaches, plums, apricots, etc., there is a substance which is called *amygdalin*. Now this substance is hydrolyzed by *emulsin,* an enzyme, into benzaldehyde, hydrocyanic acid and glucose—a mixture which has a fragrance of bitter almonds. All of which would be very fine if it were not for the presence of a rather objectionable personality — hydrocyanic acid—public poison No. 1 Benzaldehyde, on the other hand, has the almond flavor and is not poisonous.

Benzaldehyde may be prepared in many ways:

(1) By oxidation of toluene with manganese dioxide and sulfuric acid.

(2) By reducing benzoyl chloride with nascent hydrogen.

(3) By the hydrolysis of benzal chloride.

(4) By boiling benzyl chloride with aqueous lead nitrate solution.

(5) By the action of a Grignard reagent (a compound of an organic halide and magnesium, such as CH_3MgI, C_6H_5MgBr, etc.) on ethyl formate.

(6) By the destructive distillation of of a mixture of calcium benzoate and calcium formate.

Assuming that the average home lab is not supplied with a variety of the less common organic chemicals, we chose the last method of preparation. Calcium benzoate and formate can easily be prepared from the respective acids.

Prepare a solution of benzoic acid by dissolving a few grams of the acid in 25 cc. of boiling water. Then add as much calcium carbonate (precipitated chalk) as will dissolve in the boiling solution. Add in small quantities. Filter the solution while still hot to remove any undissolved solid and evaporate the filtrate to dryness to obtain crystals of calcium benzoate.

Calcium formate is prepared in the same manner using a hot, dilute solution of formic acid instead of the benzoic acid. Be careful not to spill formic acid on the skin. It produces painful burns.

Equal quantities of the two chemicals, thoroughly dried, are intimately mixed and placed in a dry test tube. Clamp the tube in an inclined position on a ring stand and fit it with a one-hole stopper and delivery tube extending to another test tube which is immersed in cold water. Heat the mixture evenly. Benzaldehyde will be formed and will pass over and con-

dense in the cool receiving tube. It can be readily recognized by its bitter almond odor.

Benzaldehyde, $C_6H_5{\cdot}CHO$, when pure is a colorless, refractive liquid boiling at $179°$. It is not very soluble in water, but is readily miscible with alcohol and ether. It is widely used in the manufacture of dyes and perfumes. If you have the patience to collect a moderate quantity of benzaldehyde, place it in a bottle, stopper tightly, and save for future experiments.

Benzoic Acid

➤ BENZOIC ACID is a colorless solid which crystallizes in needles. It is present in coal tar and in cranberries and in combination in gum benzoin and in Tolu and Peru balsams.

In the section on formaldehyde, we reacted the aldehyde with sodium hydroxide to produce a simultaneous oxidation-reduction known as the Cannizzaro Reaction. This reaction works very well with benzaldehyde to produce benzoic acid and benzyl alcohol. Prepare a concentrated solution of potassium hydroxide by dissolving 6 grams of the compound in 5 cc. of water. Cool the solution and add it to 7 cc. of *freshly distilled* benzaldehyde in a small flask. (When distilling benzaldehyde, it is a good idea to add small pieces of clay plate or glass beads to prevent bumping). Stopper the flask with a cork and shake vigorously. Do not allow the alkali solution to come into contact with your skin or clothing. A white milk-like emulsion will be formed in the flask. Set the flask aside and let it stand quietly for 12 to 24 hours.

At the end of the designated time potassium benzoate will separate out as a white precipitate. The benzyl alcohol remains in solution. Filter off the precipitate and dissolve in water. In a beaker mix together 10 cc. of hydrochloric acid with 10 cc. of water and add a small quantity of cracked ice. With constant stirring, pour the potassium benzoate solution into the cooled HCl solution. Benzoic acid will separate. Filter, wash, dissolve in hot water and recrystallize.

Benzoic acid is only slightly soluble in cold water, but readily soluble in boiling water. As with the other acids described, benzoic will form salts with alkalies, such as sodium benzoate, calcium benzoate, etc., and esters with alcohols, such as ethyl benzoate, methyl benzoate, etc.

When benzoic acid is heated with soda-lime, benzene is obtained. Mix together $\frac{1}{2}$ gram of benzoic acid with an equal quantity of soda-lime and place in a dry test tube. Heat the tube carefully and evenly, and avoid overheating and scorching. Smell cautiously at the mouth of the tube. You should be able to detect benzene by its characteristic odor.

✳   ✳   ✳   ✳   ✳   ✳

Other Organic Preparations

▶ THE HYDROCARBON compounds formed from methane, CH_4, make up the methyl series. Compounds of ethane, C_2H_6, the next member of this family of hydrocarbons, make up the ethyl series. These compounds we have studied in the preceding pages. The higher members of this paraffine family of hydrocarbons are: propane, C_3H_8; butane, C_4H_{10}; pentane, C_5H_{12}. The names of these "straight-chain" hydrocarbons then go on, following the names of the Greek numbers: hexane, heptane, octane . . .

Although propane forms the starting point for the propyl series of compounds, and butane gives rise to the butyl series, the alcohol with five carbon atoms takes the name amyl alcohol. The acid derived from amyl alcohol is called valeric acid. This is only the beginning of the complexities of naming organic chemicals.

In this section we will prepare derivatives of amyl alcohol and of some other interesting alcohols of other hydrocarbon families.

Glycerol is an example of the product formed when hydroxyl groups are attached to carbon atoms along the sides of the "chain" instead of just at the end.

Phenol differs from benzyl alcohol in having the hydroxyl group attached directly to one of the carbon atoms of the benzene ring, instead of through a methyl group.

Amyl Alcohol and Derivatives

▶ WHEN we speak of the production of alcohol by yeast-fermentation of sugars, we naturally think of ethyl alcohol. But did you know that other alcohols are also formed by this fermentation? If the ethyl alcohol is carefully separated by fractional distillation, a mixture of higher-boiling alcohols is obtained as a by-product. This mixture of alcohols is known as *fusel oil*.

Commercial amyl alcohol is obtained from fusel oil. It consists chiefly of 3-methyl-1-butanol and a smaller quantity of 2-methyl-1-butanol. These alcohols are formed from the amino acids which in turn are formed by the hydrolysis of the proteins in the yeast.

Pure 2-methyl-1-butanol is known as "active" amyl alcohol. Pure 3-methyl-1-butanol is known as *isoamyl* alcohol. The latter is the more popular and usually is the type meant when just 'amyl alcohol" is specified.

Oxidation

Ethyl alcohol is oxidized to acetaldehyde and acetic acid. Methyl alcohol is oxidized to formaldehyde and formic acid. And, similarly, isoamyl alcohol is oxidized to valeraldehyde and valeric acid.

Valeraldehyde (or more correctly, isovaleraldehyde) has a pungent apple-like odor and is used in artificial flavors and perfumes. Valeric acid (isovaleric acid), on the other hand, has a disagreeable odor somewhat like rancid cheese. Strangely enough, it is also used in flavorings and perfumes.

We will use chromic acid as our oxidizing agent. Dissolve one gram of potassium dichromate in a solution of 3 cc. sulfuric acid and 3 cc. water. After all the solid is dissolved, dilute one-half of the solution with an equal quantity of water. To this dilute chromic acid, cautiously add about 5 drops of amyl alcohol. The action will be somewhat violent and the solution turns dark green. Sniff cautiously. Do you recognize the apples? If not, heat the liquid *gently,* cool, and cautiously smell again.

Now add a few drops of amyl alcohol to the remaining stronger solution of chromic acid prepared above. Here the action will be quite vigorous, so use care. When action subsides, smell cautiously. You will probably be able to detect the pungent apple odor of isovaleraldehyde, but as the oxidation progresses, the apples become "rotten" and you will be able to detect the unpleasant odor of isovaleric acid. Again it may be necessary to heat occasionally to obtain full oxidation. But maybe you don't want to go all the way—it might be a good idea to stop when we have a good thing.

Ether

If we can produce ethyl ether by heating ethyl alcohol with sulfuric acid, isoamyl ether should be obtained when we use isoamyl alcohol. Place 10 drops of alcohol in a large test tube and add 10 drops of concentrated sulfuric acid. Heat *gently* for a few minutes. Smell cautiously, after cooling. Isoamyl ether has a pleasant fruity odor.

Esters

Most of the compounds of amyl alcohol are pleasant-smelling and find use in flavorings and perfumes. Here are a few of them for you to sniff:

Isoamyl acetate. Mix together 2 cc. of acetic acid, 2 cc. of isoamyl alcohol and 1 cc. of sulfuric acid in a test tube and heat gently for several minutes. Allow to cool. This is known commercially as "pear oil" or "banana oil." Does the odor remind you of pears?

Isoamyl butyrate. Repeat the above using butyric acid instead of the acetic acid. The result, isoamyl butyrate, has a fragrance of apricots.

Isoamyl formate. Proceed as above using formic acid in place of the butyric acid. Smell *cautiously.* It is an odd odor, not unpleasant, but it will burn your nose if you sniff too strongly.

Isoamyl salicylate. This time heat together salicylic acid with the alcohol and sulfuric acid.

Isoamyl nitrite. Place a small quantity of sodium nitrite in a test tube with one cc. of amyl alcohol. Immerse the tube in ice water and add 6 drops of concentrated sulfuric acid, a drop at a time. Stir thoroughly after each addition, and keep the tube immersed in ice water. Finally, remove the tube and add the contents to a beaker one-quarter filled with water. The amyl nitrite will separate as an oily, light green liquid. It has a penetrating fragrant odor. It should not be inhaled too strongly, as it has a marked action on the heart. It is used in medicine for the treatment of angina pectoris.

* * *

So much for our apples, pears, apricots and bananas. We hope this chemical fruit salad will not cause indigestion!

Glycerol

▶ GLYCEROL, or glycerin, is found widely distributed in animal fats and vegetable oils. These fats and oils are composed of *glycerides,* which are the esters of glycerol and fatty acids, such as palmitic, stearic, and oleic acids. When these fats are hydrolyzed (or *saponified*), glycerol is obtained. If the hydrolysis is carried out with acid, glycerol is obtained along with the above mentioned fatty acids, which are used in the manufacture of candles. If the hydrolysis is carried out with alkali, glycerol is obtained along with the sodium salts of the above mentioned acids, a mixture commonly known as soap. Thus glycerol is obtained as a by-product in the manufacture of candles and, to a larger extent, in the manufacture of soap.

During times of peace, this source of glycerol is entirely adequate. But during times of war the demand for glycerol is much greater for use in explosive mixtures, such as nitroglycerine. During World War I the excess glycerol was obtained by fermentation of sugars. In the presence of sodium sulfite, certain types of yeast convert about 25% of the sugars into glycerol. During World War II, glycerol was obtained by synthesis from propene, which is obtained from petroleum. Basically, the propene is chlorinated to form 1, 2, 3-trichloropropane, which is then hydrolyzed to obtain glycerol. We are wondering how glycerol will be obtained during World War III!

Preparation

In the home lab, the easiest method of producing glycerol is by the saponification of fats. Only we will consider soap as the by-product and glycerol as the main product. Even this method is rather difficult. Because the yield is small and the product impure, the preparation is not too practical for the home lab. Consequently, we offer this only as a demonstration experiment to illustrate an important process for your edification and, we hope, for your enjoyment.

Place 12 grams of lard, cottonseed oil, or vegetable fat (such as "Crisco") in a large beaker. Prepare a solution of 3 grams sodium hydroxide in 15 cc. of water and add it to the beaker along with 12 cc. of ethyl alcohol. Fill an ordinary saucepan about one-half full of water and immerse the beaker in the water. Heat the saucepan on the stove so that the water boils gently. Stir the contents in the beaker from time to time. If the mixture becomes too thick, add a little water. Continue heating on this improvised water bath for one hour.

Our next step is a salting-out process. Prepare a concentrated salt solution and add approximately 100 cc. to the soapy mixture in the beaker. Stir well and allow to cool. Then filter off the particles of soap. The glycerol is present in the filtrate.

Neutralization is next in order. Drop a piece of blue litmus paper in the solution (the filtrate). Stirring constantly, add hydrochloric acid, drop by drop, until the litmus paper just turns pink.

Finally, we must separate the glycerol from the salt. To do this, evaporate the solution to dryness, using the improvised water bath described above, or one of your own design.

Add 15 cc. of absolute ethyl alcohol to the residue. Stir thoroughly, then allow the solid matter to settle. Carefully pour off the clear alcohol solution and again evaporate to *near* dryness. The residue remaining is glycerol.

Reactions

When glycerol is dehydrated, *acrolein* is formed. Place one gram of powdered potassium bisulfate in a dry test tube and add about 6 drops of glycerol. Heat the mixture for a few moments and smell *cautiously*. The pungent, irritating odor indicates the presence of acrolein.

Prepare a solution of borax and color it blue with litmus. Upon the addition of glycerol, the solution turns pink. This is due to the presence of boric acid which is liberated from the borax by glycerol.

Glycerol is readily oxidized. Place a drop of glycerol in a metal pan. Sprinkle a "pinch" of finely powdered potassium permanganate on top of it. The oxidation is so rapid that the mass is ignited and burns with a blue flame. Use only small quantities and keep your face away.

In aqueous solution, the oxidation products of glycerol are quite numerous. For example, hydrogen peroxide in the presence of ferrous sulfate, forms first glyceraldehyde and then, as further oxidation proceeds, 3-hydroxy-2-oxopropanal, 2-oxopropanal, oxalic acid, formic acid, and carbon dioxide.

Uses

The properties of glycerol make it useful for many purposes. Because it is non-volatile and hygroscopic, it is used in printing inks, inking pads, and in tobacco to keep it moist. Because of its sweet taste, it is used in confectionery, beverages, and preserves. Because of its softening effect, it is used in cosmetics, lotions, liquid soaps, etc. Because of its low freezing point and solubility in water, it is used as an anti-freeze in automobiles. The trinitrate of glycerol (nitroglycerin) is used in the manufacture of dynamite. The esters of glycerol are used as emulsifying agents, synthetic resins and waxes.

From hand lotions to dynamite, here is one by-product that really pays off!

Phenol

➤ THE VERY important phenol, or carbolic acid, is present in coal tar. In fact, it was originally obtained from coal tar. But it became so useful in the preparation of medical and industrial compounds, dyes, and resins that the coal-tar supply was no longer adequate. So the chemist had to devise other means of producing the compound.

The technical definition of a phenol is "a derivative of benzene which contains one or more hydroxyl groups (OH) attached directly to carbon atoms of the nucleus." Thus, we have the formula of benzene as C_6H_6. Replacing one hydrogen with one hydroxyl group, we have a monohydroxybenzene, C_6H_5OH, which we know as phenol. Using two hydroxyl groups, we obtain dihydroxybenzenes, such as *catechol*, $C_6H_4(OH)_2$; *resorcinol*, $m\text{-}C_6H_4(OH)_2$; and *hydroquinone*, $p\text{-}C_6H_4(OH)_2$. Or, replacing

with three hydroxyl groups we have *pyrogallol,* 1-2-3-$C_6H_3(OH)_3$;*phloroglucinol,* 1-3-5-$C_6H_3(OH)_3$; and *hydroxyquinol,* 1-2-4-$C_6H_3(OH)_3$.

It would appear from the above that the logical compound to use in the preparation of phenol would be benzene. And so it is used. In one process the benzene is sulfonated to obtain benzenesulfonic acid, which in turn is converted to the sodium salt. The sodium benzene-sulfonate is treated with molten sodium hydroxide to obtain sodium phenoxide. The phenol is liberated from the phenoxide by carbon dioxide or sulfur dioxide.

In another process (the Dow process) the benzene is chlorinated to form chlorobenzene. This compound is mixed with diphenyl oxide and sodium carbonate and subjected to heat and pressure to obtain the phenol.

Still another process converts chlorobenzene to phenol by forcing it with steam over a silica gel preparation at high temperatures.

In the laboratory, it is most convenient to prepare phenol from aniline by a process of diazotization followed by hydrolysis. As you know, the aniline itself is obtained from nitrobenzene which in turn is prepared from benzene.

First it is necessary to convert the aniline to the sulfate. Place 40 cc. of water in a beaker. Slowly add 6 cc. of sulfuric acid. Stir the solution, and while still warm, add 5 grams of aniline. Continue stirring until the aniline sulfate dissolves and a clear solution is obtained. If necessary, warm the solution gently.

Bring the temperature of the solution down to 5 degrees by immersing the beaker in a mixture of cracked ice and salt. Dissolve 4 grams of sodium nitrite in a small quantity of water and add it slowly to the cooled aniline sulfate solution. Add only a small quantity at a time, stirring after each addition. You should allow about ten minutes to complete this reaction. This process is known as *diazotization,* and the compound obtained is benzene diazonium sulfate. Whenever you experiment with diazotization reactions, be sure to follow instructions carefully. These compounds, are tricky, and in the dry state there is some danger of explosion.

After all the nitrite has been added, allow the beaker to remain in the ice bath for about five minutes. Then transfer the liquid to a large flask. Heat gently to a temperature of 50 degrees. At this point nitrogen is evolved and the reaction should proceed of itself without further heating. During this reaction the phenol separates as a dark-colored oil. After all action ceases, carefully draw off the oil with a medicine dropper. This is crude phenol.

Dissolve as much of the oil as possible in water by boiling and stirring rapidly. Add some of the solution to a solution of ferric chloride. A violet coloration is obtained which identifies the phenol.

Mix a small quantity of phenol solution with hydrochloric acid and add a few drops of concentrated nitric acid. A red color is formed.

Add a few crystals of sodium nitrite to phenol solution along with a solution of mercurous nitrate. Boil for a short time. A red color is obtained. This is an extremely sensitive test for phenol.

Dissolve a crystal of sodium nitrite in 3 cc. of concentrated sulfuric acid. Add a small quantity of phenol (about ½ gram). A brown solution is obtained at first which quickly changes to blue. If you pour this liquid into water, it will turn red. If you add sodium hydroxide solution it will turn greenish-blue.

Phenol Resins

Phenol is used in the manufacture of various resins and plastics. With formaldehyde, it forms the popular *Bakelite*. You can prepare several of these resins in the home laboratory, but we suggest you use purified crystals of phenol rather than the crude oil obtained in the experiment. You can, of course, purify the oil if you wish by a process of steam distillation.

The distillate is saturated with salt and the phenol extracted with ether. This is a rather elaborate operation not too well suited for a home laboratory. For detailed instructions on the preparation of Bakelite, see page 60.

Another resin can be obtained by using hexamethylene tetramine, which is a compound made from formaldehyde. Mix 3 grams of phenol with ½ gram of hexamethylene tetramine. Warm the mixture very slowly until complete solution of the compounds is obtained. Then heat to 150 degrees, at which time ammonia is formed. Remove the heat and allow the action to proceed by itself. After all action ceases, allow to cool. The plastic obtained can be worked into any shape desired before it hardens.

Picric Acid

➤ PICRIC ACID is a versatile compound with a three-fold personality. It serves as a dye, an antiseptic, and an explosive. During the first World War picric acid was used to treat the wounds that picric acid caused.

Picric acid forms bright yellow crystals. It is only moderately soluble in water, more so in alcohol or benzene. It was obtained by the action of nitric acid on indigo as early as 1771. It was introduced as a yellow dye for silk in 1849, as an explosive in 1871 and later as a bactericidal agent in the treatment of burns.

Preparation

Picric acid, or trinitrophenol, is obtained by the sulfonation of phenol and then treating the resultant product with nitric acid. The direct action of nitric acid upon phenol will result in the oxidation of the phenol rather than nitration. Hence the reason for sulfonating phenol first to obtain primarily p-phenolsulfonic acid. The latter is then nitrated to form trinitrophenol.

Place 2 grams of phenol (carbolic acid) crystals in a dry flask. Add 2.5 cc. of concentrated sulfuric acid, and mix thoroughly by shaking the flask. Now heat the mixture on a water bath for about 15 or 20 minutes. This can easily be accomplished by immersing the flask part way in a large evaporating dish filled with boiling water. Do not attempt to heat the flask directly.

Next, *thoroughly* cool the mixture by immersing the flask in ice water. When cool, place near an open window and cautiously add 7½ cc. of

concentrated nitric acid. A violent reaction will take place and large volumes of brown fumes will pour out of the flask. Although vigorous, the action is harmless. Take care, however, not to inhale the brown fumes. After the action subsides, heat again on a water bath for ½ hour. Then add 25 cc. of water and immerse the flask in ice water. A brilliant yellow precipitate of picric acid will separate. Filter the crystals and wash thoroughly with water. Finally, recrystallize from a mixture of one part of alcohol and two parts of water. Do not attempt to dry the crystals.

Picric acid explodes when rapidly heated or by percussion! Therefore keep the compound damp. If you care to save it, we suggest you keep it in aqueous solution. Commercially picric acid contains about 10-20% added water for safety.

Reactions

The dyeing qualities of picric acid can easily be demonstrated by immersing a piece of silk or wool in a moderately concentrated solution. The cloth will be colored a brilliant yellow. Picric acid also stains the skin yellow, as perhaps you have noticed if you have not been working carefully.

When picric acid is heated with chlorinated lime solution, chloropicrin is formed and can be detected by its pungent odor. Chloropicrin was one of the poison gases used during the first World War. It acts as a lung irritant, causing severe coughing, crying and vomiting.

Picric acid forms many colorful compounds. Here are just a few of them.

Add a solution of copper sulfate to a solution of picric acid, and pour in a little ammonia. A beautiful green color is obtained, consisting of hexagonal shaped crystals which polarize light. This reaction serves as a delicate test for picric acid.

To a solution of stannous chloride, add enough sodium hydroxide to dissolve the precipate formed, then add the clear solution to aqueous picric acid. A reddish-tan precipitate is obtained.

On adding zinc and dilute sulfuric acid to picric acid, a yellowish-red liquid is formed. If this be added to alcohol and filtered, it will eventually turn green, then blue, and finally violet.

A blood-red color is obtained by heating picric acid with sodium hydroxide and potassium cyanide. (*Potassium cyanide is deadly poisonous. It must be handled with extreme care!*)

When heated with potassium ferrocyanide, picric acid produces a sky-blue color. This will gradually change to red-violet.

Epitaph

With the advent of many efficient synthetic dyes, picric acid no longer is used in this capacity.

And with the coming of the atom bomb, it is outmoded as an explosive.

Finally, with the introduction of penicillin and sulfa drugs, its use in the medical field is being curtailed.

Poor picric acid! It has seen better days!

$\star \quad \star \quad \star \quad \star \quad \star \quad \star$

Synthetic Dyes

> OF ALL the synthetic materials produced through organic chemistry today, the dyes are perhaps the widest used, of the greatest variety, and the most available. The modern dye industry began in 1856 when Perkin accidentally discovered the lilac-colored mauve from aniline. Of course, this discovery spurred further research for other dyes and in 1859 magenta was synthesized. Then in 1869 alizarin was made synthetically, which was the first dyestuff to be so honored. From this time on progress was rapid and today there are hundreds of synthetic dyes available of all types, colors, shades, and hues.

The synthetic dyes are produced primarily from crude material obtained from coal tar, such as benzene, naphthalene, and phenol. From these substances the "intermediates", such as aniline and anthraquinone, are prepared. Finally, the intermediates are treated with the proper reagents to produce the dyes.

Aniline

> IT WAS IN 1826 that the chemist, Unverdorben, distilled indigo and obtained a new compound. But little was learned concerning the new compound and it was not considered to be of much value.

Eight years later the chemist, Runge, obtained the same compound from coal tar. But, again, little was known about it and it was considered more or less useless.

But in 1856 the chemist, Perkin, while searching for a method to prepare quinine synthetically, accidentally discovered a use for the substance. During the course of his research, he poured chromic acid in a container which held some of the "useless compound" obtained from coal tar. No doubt he was greatly surprised to see the deep violet color which diffused rapidly throughout the container. This was *mauve,* the first of the many colorful aniline dyes, which the chemist now prepares from black, sticky, foul-smelling coal tar.

You can prepare aniline in the home laboratory and repeat Perkin's experiment. This can be done using benzene as the starting point, from which nitrobenzene is prepared. The nitrobenzene is then reduced to aniline with nascent hydrogen.

Carefully mix together 3 cc. of concentrated sulfuric acid and 3 cc. of concentrated nitric acid. Cool the solution and add it in small portions to 2 cc. of benzene in a small flask. Shake the flask thoroughly after each addition. When all has been added, warm

| Benzene | Nitrobenzene | Aminobenzene (aniline) |
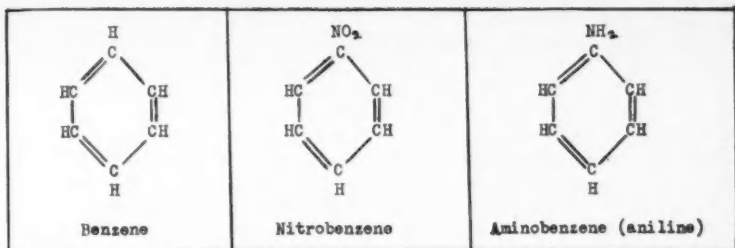
the flask *gently* for a few minutes. Nitrobenzene is formed and can be recognized by its characteristic almond-like odor. Inhale cautiously as the vapors are poisonous. Pour the mixture into 10 cc. of water in a test tube. The nitrobenzene will separate as a light yellow oily liquid. Transfer this liquid to another test tube by means of a medicine dropper. Add a small piece of tin and 5 cc. of hydrochloric acid. If the reaction is too slow, it can be hastened by gentle heat. (Shake the tube occasionally). Nascent or atomic hydrogen is liberated and reduces the nitrobenzene. The light yellow liquid gradually turns darker in color. If necessary add more tin or acid to assure ample generation of hydrogen. The aniline obtained in this manner is dark brown with a benzene-like odor.

The chemistry of the above reactions can easily be understood if the formula for nitric acid is visualized as ON.NO$_2$. Now the hydroxyl radical (OH) has a strong attraction for the hydrogen atom (H). The latter is readily available in the benzene molecule. (Refer to accompaning diagram.) Thus the two unite to form a somewhat common substance with the formula, H$_2$O. This leaves the nitro group (NO$_2$) alone, which immediately combines with the carbon from which the hydrogen was snatched by the hydroxyl group. The new combination is nitrobenzene. When aniline is formed, the oxygen in the nitro group is replaced by hydrogen to form the amino (NH$_2$) group. The oxygen that is set free immediately combines with more of the hydrogen to form the substance H$_2$O. And that's all there is to it! Nothing really complicated about it, is there?

Mauve

The beautiful mauve dye is formed when an oxidizing agent is added to aniline. Perkin used chromic acid, but bleaching powder is generally used now because it is cheaper and more readily available. Stir about one teaspoonful of bleaching powder (chloride of lime) in 200 cc of water. Add to this one drop of aniline. Immediately the purple color is formed and gradually spreads throughout the solution. Filter, and take notice of the clear solution. It will appear wine-red in strong light. Various dilutions will

produce many lovely hues of violet. Before disposing of the dye, add a solution of sodium bisulfite to it. Perhaps the result will surprise you!

Rosaniline

➤ ROSANILINE is the color base of magenta or fuchsin. It was first prepared by Verquin in 1859 by oxidizing aniline with stannic chloride. The resultant red dye was named "fuchsin". Later the chemist Hofmann claimed that he had obtained the same compound by treating aniline with carbon tetrachloride, which he named "rosaniline".

You can best demonstrate these experiments in the home laboratory by using mercuric chloride. Place a small quantity of this compound in a dry test tube. Add a few drops of aniline and heat very gently for a few minutes. Finally, dissolve the product in alcohol and add a few drops of hydrochloric acid.

Actually there are several rosaniline dyes. The rosaniline of commerce is prepared by oxidizing equimolecular amounts of para and ortho toluidine.

Aniline Black

➤ PERHAPS you have noticed that we have done nothing to prepare dyes thus far except to add an oxidizing agent to aniline. With bleaching powder we obtained mauve, with mercuric chloride we obtained rosaniline and now we will use chromate solution to produce aniline black. There are several compounds and mixtures of compounds known as "aniline black". The one we obtain by oxidation has already been described in the chapter on "Oxidation".

The first aniline black was prepared in 1862 by Lightfoot. Aniline hydrochloride was heated with an oxidizing agent, an oxygen carrier, and a hygroscopic salt. Suppose we try this. Place in a test tube equal quantities of aniline and hydrochloric acid (to produce aniline hydrochloride), potassium chlorate (the oxidizing agent), copper chloride (the oxygen carrier), and ammonium chloride (the hygroscopic salt). Mix thoroughly together, and add about 10 or 20 cc. of water. Warm gently.

Aniline black is one of the fastest and most beautiful black dyes known today. To the best of our knowledge, its exact constitution has not yet been established.

Naphthol Yellow

➤ WHEN bituminous or soft coal is heated to a high temperature in a sealed retort a thick, tarry black liquid condenses which is known as *coal tar*. Perhaps you have heard of it.

When the coal tar is distilled, a number of important compounds are obtained. Included in the fraction which distils over from 110° to 205° is an acid oil and crude naphthalene. As this mixture cools, the naphthalene crystallizes out and is removed and purified.

Now when naphthalene is sul-

fonated (treated with sulfuric acid) at 0°, a compound known as a-naphthalene-sulfonic acid is obtained. The sodium salt of this acid is fused with sodium hydroxide to form a-naphthol. When a-naphthol is sulfonated and then nitrated a compound known technically as 2, 4-dinitro-1-naphthol-7-sulfonic acid, more commonly known as *naphthol yellow*, is obtained.

So, there you have it. Simply obtain a piece of soft coal and get to work!

But for those who do not wish to go all the way back to the coal (including us), we suggest using a-naphthol as the starting point. Obtain a good grade of said chemical, and place 2 grams of it in a small flask. Add to this 5 cc. of concentrated sulfuric acid. Heat the mixture by immersing the flask in a larger container of boiling water. Keep the water boiling vigorously. The mixture in the flask should attain a temperature of 120°. Continue heating for 15 minutes; then cool and pour the contents into 15 cc. of water in a beaker. The first step of sulfonation is now completed.

Next we proceed to the nitration process. Cool the solution to around 25° by immersing the beaker in cold water. During the nitration process, it is essential that the temperature of the liquid does not rise above 40°. It might be advisable to add a little ice to the water in which the beaker is immersed. Now add to the mixture 3 cc. of concentrated nitric acid, *a few drops at a time*. Stir the solution vigorously during the addition of the acid. This is rather tiresome, and if you have a mechanical stirrer, it certainly will be useful here. After all nitric acid has been added, continue stirring for about 30 minutes. Then allow the solution to stand for 24 hours while you recuperate.

After a day or so, naphthol yellow will crystallize out of the solution. Now you can either extract the acid as is, or you can prepare the potassium salt in which form it is available commercially.

To obtain the acid, carefully pour off the liquid and transfer the crystals to another container of water. Heat to boiling for a few minutes, then filter. The deep intense yellow solution of naphthol yellow is obtained as the filtrate.

To obtain the potassium salt, separate the crystals by filtration. Wash them with a small quantity of saturated sodium chloride solution. The crystals are then dissolved in the smallest possible quantity of hot water. Next prepare a concentrated solution of potassium carbonate and add it to the hot naphthol yellow until the solution just barely reacts alkaline with litmus. The orange-yellow crystals of the potassium salt will separate out on cooling. They can be filtered off and dried.

Naphthol yellow is used for dyeing wool and silk; for coloring foods and cosmetics.

Fluorescein

➤ Now we will consider the preparation of the phthalein of resorcinol (*resorcinolphthalein*). This interesting and colorful compound is more commonly known as *fluorescein*.

Informal Preparation: Small quan-

tities can be prepared quickly and easily by the following method:

In a large test tube place a small quantity, about ½ gram, of resorcinol (resorcin) and one-half as much (¼ gram) phthalic anhydride. Add 10 drops of concentrated sulfuric acid, and heat the mixture to boiling for two or three minutes. Then *carefully* pour the hot mixture into a beaker containing 15 cc. of water. The crude fluorescein separates as a yellowish-red precipitate. The product prepared in this manner is very crude, but it will be sufficiently pure for our purposes.

Multi-Colors

Pour a little of the suspended fluorescein in a test tube and add a solution of sodium hydroxide. Heat gently to dissolve the precipitate, then filter. Examine the filtrate. Hold it at different angles in respect to transmitted and reflected light. You will note that the solution is yellow by transmitted light and green by reflected light. Now heat the solution again and add about 2 cc. of dilute hydrochloric acid. Again note the color change.

Actually, the alkaline solution is a sodium salt of fluorescein, sometimes known as Uranine Yellow, and is soluble in water. Fluorescein itself is insoluble in water.

Formal Preparation

Because of its rather unusual properties, you may wish to prepare fluorescein in larger quantities for further experimentation. If so, it is advisable to use zinc chloride instead of the sulfuric acid as described above.

Place in a large beaker five grams of phthalic anhydride and seven grams of resorcinol. Heat the mix-

ture to 180°, preferably in an oil bath if possible. When this temperature is reached, add in small portions four grams of pulverized fused (anhydrous) zinc chloride.* Stirring occasionally, continue heating until the mixture becomes solid. This will usually require about one hour, more or less. Then cool and scrape the solid mass from the beaker. Pulverize in a mortar and boil the powder in a solution of five cc. hydrochloric acid and 75 cc. water. Finally, filter the fluorescein, wash and dry. Again the product is not pure, but sufficiently so for the preparation of eosin. However, if you desire, further purification can be obtained by dissolving the fluorescein in hot dilute sodium hydroxide, and reprecipitating with acid.

Eosin

Eosin (tetrabromofluorescein) is used as a dye, usually in the form of its sodium salt which is soluble in water. To prepare it, shake one gram of fluorescein in six cc. of 95% alcohol. Carefully add, drop by drop, about one-half cc. of bromine. The fluorescein will gradually dissolve to form first the soluble dibromofluorescein and finally the insoluble tetrabromofluorescein. If the latter is not precipitated, add a few additional drops of bromine. Pour the mixture into 15 cc. of water, stir and filter off the eosin. Suspend the crude eosin in water and add dilute sodium hydroxide solution until entirely dissolved. Now pour the solution into 10 cc. of boiling water to which one cc. of hydrochloric acid has been added. Finally, filter off the orange-red eosin.

To prepare the soluble sodium salt

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* For preparation of this product, see page 45, "Malachite Green."

of eosin, mix thoroughly together in a mortar one gram of dry eosin with $\frac{1}{3}$ gram anhydrous sodium carbonate. Make into a paste with ethyl alcohol. Add one cc. of water, transfer to a test tube and heat gently until evolution of gas (CO_2) ceases. Then add five cc. ethyl alcohol, heat to boiling and filter the hot solution. Allow the filtrate to stand. Eventually, green-red iridescent needles of the sodium salt will crystallize out of solution.

This is the commercial form of eosin which is used in red ink, as a dye for wool and silk, and as coloring for lipstick and nail polish.

As stated previously the sodium salt of eosin is soluble in water. The concentrated solution is deep brownish red whereas the dilute solution is yellowish-red with greenish fluorescence.

Preparation of Bromine

If you do not have bromine, the small amount needed for preparing eosin can easily be made. Simply mix together equal quantities (not more than one gram each) of potassium bromide and manganese dioxide in a test tube. Add one cc. of sulfuric acid and attach a delivery tube leading to another test tube immersed in a beaker of ice water. Heat gently. Bromine is liberated and will condense in the cool receiving tube. *Be very careful not to inhale the fumes or spill the liquid on the skin.*

Malachite Green

➤ For the synthesis of Malachite green, we need 3 cc. of *freshly distilled* benzaldehyde. Use care in performing this distillation. It might be a good idea to add a few pieces of porcelain plate or glass beads to the benzaldehyde in order to prevent "bumping" and uneven boiling.

Next we must prepare *anhydrous* zinc chloride. Place 5 grams of the compound in a large porcelain evaporating dish. Heat gently at first with constant stirring. Gradually apply more heat and finally enough to melt the compound. Continue to heat for a few minutes, then cover the dish with a glass plate and allow to cool. Add to the cooled zinc chloride, the 3 cc. of freshly distilled benzaldehyde prepared above along with 6 cc. of dimethyl aniline. Heat the mixture on the steam bath for 90 minutes.

You can devise your own "steam bath" by using a large beaker on which the evaporating dish can set comfortably, on top, without falling in. Fill the beaker half full of water and heat. The steam from the boiling water will heat the dish. Of course, arrange the dish so that the lip of the beaker remains open to allow excess steam to escape. Cover the evaporating dish with a glass plate. Stir the contents frequently during the heating and if the mixture becomes thick, add a little hot water.

The product we obtain is known as the *leuco-base* of Malachite green, or, if you prefer, tetramethyldiaminotriphenylmethane. Our next step is to convert it to the carbinol (color) base by oxidation.

Dissolve the residue in a solution of 3 cc. hydrochloric acid and 6 cc. of water. Transfer the liquid to a large beaker. Add 100 cc. of water and about 20 grams of cracked ice. Now prepare a suspension of lead dioxide,

PbO_2, by vigorously shaking 2 grams of the powder in 15 cc. of water. This is our oxidizing agent. Add it to the beaker slowly, in small portions, stirring continuously.

The next step is to remove the lead. This is done by adding a solution of 2 grams of sodium sulfate in 10 cc. of water. Filter off the resultant lead sulfate.

Malachite green is usually precipitated as the double salt of the hydrochloride and zinc chloride.

Add to the filtrate a solution of 3 grams zinc chloride dissolved in 15 cc. of water followed by 12 grams of solid sodium chloride. Stir thoroughly for a few minutes. Filter off the green crystals and carefully dry. If you have worked carefully, you should have a yield of about 3 grams.

Prepare to Dye

Now that you have obtained Malachite green, are you prepared to dye?

Prepare a solution of Malachite green by dissolving a small quantity of the powder in water. Heat to boiling and immerse a piece of wool or silk in the hot solution for several minutes. Remove and wash with water. The cloth is dyed a deep blue-green. This process is known as *direct dyeing*.

As you have certainly observed by now, the dye is an intense blue-green color—and a little goes a long way. It is a basic dye and will dye wool and silk directly. However, in order to dye cotton, the cloth must be mordanted first. By "mordanted" we mean treated with a substance ("mordant") which is taken up by the fibers of the cloth. The mordant in turn takes up the dye. Thus I

suppose you could say that we actually dye the mordant, not the cloth. But who knows the difference?

The Mordant Process

If you will perform the above operation with cotton you will find the color is not fast. To dye cotton preliminary treatment with a mordant is necessary. This process is known as *mordant dyeing*. (For best results with cotton, it is advisable to boil it for 10 minutes in a solution of one gram sodium carbonate in 500 cc. of water then rinse several times in clear water, before attempting to dye it.) Dissolve a very small quantity of tannic acid (about 0.2 g.) in 100 cc. of water. Heat to boiling and immerse a piece of cotton cloth in the hot solution for several minutes. Remove the cloth, press it with a spoon to remove excess liquid, then immerse for several minutes in boiling Malachite green solution. You will note this time that the dye is fast. To make the color somewhat darker, the tannic acid may be fixed to adhere more strongly to the fibers. This is done by dipping the cloth in tannic acid as before and then immersing in a solution of tartar emetic for about 10 minutes. Use about 0.2 g. of tartar emetic dissolved in 200 cc. of water.

Malachite green is converted into a colorless compound by reducing agents. This can be demonstrated by adding a solution of sodium bisulfite to the dye. Incidentally, this is a good method of removing the dye from your glassware ... (or from your hands?)

Well, we hope you have enjoyed dyeing. If so, we must dye again some time.

Methyl Violet

> SUPPOSE we now move to the lower side of the rainbow for a lovely violet color.

Methyl violet is another dye obtained from the black, sticky, foul-smelling coal tar. From the coal tar we obtain benzene. Subjecting the benzene to nitration, we obtain nitrobenzene. The nitrobenzene is reduced to form aniline. And from aniline and its derivatives we obtain a multitude of dyes — all colors of the rainbow in various shades and hues. One of these derivatives is *dimethylaniline*, which we will use in preparing Methyl violet. Dimethylaniline is prepared by heating aniline, methanol and sulfuric acid under pressure.

We will use dimethylaniline as our starting point. You should be able to purchase this reagent from one of the laboratory supply houses in our larger cities.

Methyl violet is formed by heating phenol and dimethylaniline with sodium chloride and cupric sulfate. Mix 65 grams of finely powdered sodium chloride with 5 grams of finely powdered cupric sulfate. Common table salt may be used if it is pulverized by grinding in a mortar. The cupric sulfate should also be ground in a mortar. Sift the thoroughly mixed powders into a large dry beaker.

Next, prepare a solution of phenol (carbolic acid) by adding 4 grams of the reagent to 15 cc. of water. (Do not allow phenol to come in contact with your skin as it can cause a serious burn.) As all of the phenol will not dissolve in this quantity of water, just heat the solution until the solid crystals melt. Pour into the beaker

containing the mixed salt and cupric sulfate, stirring constantly. You will end up with a light green watery paste. To this add 10 cc. of dimethylaniline and continue to stir. Transfer the mass to a large Florence flask and heat to a temperature of 60 degrees. Keep the solution at this temperature for three hours, or even longer if you have the time.

By now you will begin to observe the violet coloration as Methyl violet is formed in the solution. Allow the mixture to cool and then transfer the mass (or should we say mess?) to 300 cc. of boiling water to which 4 grams of calcium oxide has been added. Allow this mixture to boil until it is fairly free from lumps — about one half hour — and allow to cool. The dye separates out of solution as a dark greenish-purple mass. Transfer a small portion of it to some alcohol in a beaker. The lovely shade of violet is indicative of Methyl violet.

As you no doubt have noticed by this time, the violet color of the dye is quite intense. You can dilute the alcohol solution many times and the purple color will still be present. In fact you will find that it is exceedingly difficult to clean your glassware. The purple color just lingers and lingers. By the time you are through we wager that you'll be quite tired of the "lovely" violet color! Rinsing your glassware with alcohol will help remove the dye. Try not to get it on your hands, as it is somewhat difficult to remove therefrom, as we have discovered from experience.

Methyl violet is used in certain inks and for dyeing wool, silk, and mordanted cotton. It is not fast to light.

Crystal violet, similar to Methyl violet but less reddish in color, is prepared by heating Michler's ketone (4,4′-Bis-dimethylamino-benzophenone) with dimethylaniline and phosphorous oxychloride. This compound mixed with Methyl violet forms the well-known *Gentian violet.* Gentian violet is used as an antiseptic for infected wounds.

Monastral Blue

➤ In 1928 the workers in the Grangemouth Works of Scottish Dyes, Inc. were very much surprised, perhaps disconcerted, to find that several batches of phthalimide they were preparing had a bluish tint. Since phthalimide is normally white, they deduced that some foreign substance was causing the blue coloration. An investigation revealed a pin hole in the porcelain lining of the iron vessel and the contact with iron resulted in the formation of a blue pigment.

Thus, by accident, was discovered the series of compounds known as *phthalocyanimes* including the excellent blue pigment, copper phthalocyanime, or 'Monastral Blue." They are readily formed by the action of metals or metallic salts on phthalonitrile.

Copper phthalocyanime (Monastral Blue) is a deep indigo-blue pigment. It is very stable and is not affected by alkalies, heat or light. It is insoluble in most of the usual organic solvents. It absorbs the yellow and red portions of the spectrum almost completely, thus making it a practically "true" blue color.

We can prepare the pigment in the home laboratory from urea, phthalic anhydride, and cupric chloride. The ingredients are heated to a temperature of 200 deg. in an oil bath.

First, prepare the oil bath by filling a 250-cc. beaker one-half full with vegetable shortening, such as Crisco, Spry, or similar preparation. Apply gentle heat until the fat is completely melted. Next weigh out 4 grams of urea and transfer it to a *dry* 60-cc. Florence flask. Add a "pinch" of boric acid and mix the powders. The boric acid serves as a catalyst. Immerse the flask inside the beaker of fat until the round portion is completely submerged. In this position the neck is fastened to the ring stand by a clamp. Do not allow the flask to touch the beaker. It should be entirely suspended in the liquid fat. Place a thermometer in the flask, and apply heat to the beaker. Continue to heat until the contents of the flask reach a temperature of 150 deg. At this point the urea will melt and fumes of ammonia will be driven off. Now mix together 3 grams of phthalic anhydride with one gram of cupric chloride. If your phthalic anhydride is lumpy, powder it first in a mortar. Sift the mixed powders into the molten urea in the flask and stir. Continue to heat, with frequent stirring, until a temperature of 200 degrees is reached. There will be some frothing and fumes will be given off. Do not inhale these fumes (It is always a good idea to experiment in a well-ventilated room). The mixture at first is blue, then turns to deep green, and finally back to blue again with a purple copper luster. Continue heat-

ing at 200 degrees until the mixture becomes dry, which should require about 20 minutes.

Carefully remove the flask from the oil bath and allow to cool. Scrape the blue crystals into a mortar and grind to a fine powder. This is the crude pigment. Try not to get any of it on your hands.

The compound should now be purified. First mix the powder with dilute sodium hydroxide solution. Warm gently for a few minutes, then filter. Wash the precipitate thoroughly with water. Next, mix it with dilute hydrochloric acid and repeat the procedure — warm, filter, and wash. This time allow it to dry. Dissolve the finely powdered dry pigment in concentrated sulfuric acid. A deep green solution results. Carefully pour this solution, in a thin stream, into a beaker of water with continual stirring. The pigment separates out as a beautiful blue precipitate. Finally, filter and dry.

As stated above, Monastral Blue is insoluble in the common solvents. In addition to cold concentrated sulfuric acid, it will dissolve in boiling quinoline and a-methylnaphthalene, and that's about all. Since you have a flask that is no doubt very badly stained, cleaning poses a real problem. We suggest that you throw the flask away rather than attempt to clean it.

The stability of Monastral Blue makes it an excellent pigment. It is one of the best for 3-color process used in color printing. It is also used in coloring paper, leather, printing inks, artists' colors, paints, lacquers, and the bindings of books.

Comparatively speaking, Monastral Blue is a rather recent addition to the growing list of purely synthetic dyes. Aside from its properties as a dye, it has a structural formula which is quite interesting to chemists. This formula has been found to be closely analogous to that of a green pigment —chlorophyll. In chorophyll the metalic element is magnesium instead of copper. The accidental discovery of the phthalocyanimes is another step toward solving the mystery of that fascinating, life-giving, elusive chlorophyll!

Aniline Yellow

➤ HERE IS an experiment in progressive synthesis which will test your skill as a home chemist. By "progressive synthesis" we mean the preparation of one compound and then using this to prepare another, and so on until the final product is obtained. Obviously, it is important to prepare each compound most carefully so that it will work successfully in succeeding syntheses.

We will prepare two compounds, diazoaminobenzene and aniline hydrochloride, and then combine them to form the third, aminoazobenzene. Hence, all of the experiment is divided into three parts:

Preparation of Aniline Hydrochloride

Mix together in a beaker 5 cc. of aniline with 5 cc. of water. Slowly add 10 cc. of concentrated hydrochloric acid, with stirring. Heat the mixture gradually until it just begins to boil; then allow to cool. Filter off the crystals which form rapidly as the

liquid cools. Finally, carefully dry the crystals. This can best be done by heating on an improvised steam-bath. Scrape the crystals from the filter paper onto a watch glass. Place the glass over the top of a beaker half-filled with water. Heat the water to boiling so that the steam will rise and heat the watch glass. Arrange the glass so that the excess steam escapes through the spout of the beaker. When dry, cover the crystals and save for use later on.

Preparation of Diazoaminobenzene

Place in a 125-cc. Erlenmeyer flask a mixture of 2½ cc. concentrated hydrochloric acid in 50 cc. of water. Add 2 cc. of aniline and stir until dissolved. Then cool the solution to about 25 degrees. (If necessary immerse the flask in a container of cold water). Keeping the temperature between 25 and 30 degrees, carefully add one gram of finely powdered sodium nitrite in small portions. Shake the solution after each portion. A brown colored precipitate forms. Allow to stand for five minutes, then add a solution of 2½ grams crystallized sodium acetate dissolved in 10 cc. of water. Again shake thoroughly and allow to stand for 15 minutes. This time a dark yellow precipitate is obtained. Filter it off and wash with cold water. Now it is necessary to dry the product. This must be done *very carefully* as diazoaminobenzene explodes when heated to 150 degrees. We suggest using the steam bath described above for this purpose. Heat until the compound is *nearly* but not entirely dry, then let it stand in a warm but not hot place until it is entirely dry. The product is to be used immediately in the final step. Do not attempt to store it.

Preparation of Aminoazobenzene

Now take one gram of the dry aniline hydrochloride prepared in part 1 along with the entire amount of diazoaminobenzene (which should be close to two grams) prepared in part 2 and dissolve both in 5 cc. of aniline in a test tube. Heat the mixture for about 30 minutes at 30 degrees and then for an additional 30 minutes at 45 degrees. Insert a thermometer in the test tube and stir frequently throughout the heating. Of course, only a small amount of heat is required to maintain the temperature. Be careful not to overheat. Next a solution of 6 cc. concentrated hydrochloric acid in 18 cc. of water is added with stirring, and the mixture cooled. Aminoazobenzene hydrochloride separates out of solution. Filter it off and wash with dilute hydrochloric acid. Dissolve the product in 100 cc. of hot water to which a little hydrochloric acid has been added. Filter again and add 5 cc. of concentrated hydrochloric acid to the filtrate. Cool, filter off the precipitate and wash once more with dilute hydrochloric acid. This compound, aminoazobenzene hydrochloride is known as Aniline Yellow. It colors silk and wool an intense yellow. You can try it by dipping the material in a hot solution of aminoazobenzene hydrochloride which has been made slightly acid.

The free base, aminoazobenzene, can be obtained by adding one gram of the hydrochloride to 4 cc. of alcohol. Add ammonium hydroxide until it dissolves. The base is precipitated by adding water and can be obtained by filtering.

Phenolphthalein

➤ No DOUBT you are acquainted with phenolphthalein through the lovely pink color it forms with alkalies. It is formed when phenol is heated with phthalic anhydride and a dehydrating agent. Phthalic anhydride, which you can buy from your chemical supply house for this experiment, is made by heating phthalic acid, which is formed by oxidation of naphthalene.

Place in a small flask 3 g. of phthalic anhydride, 6 g. of phenol (carbolic acid) and 2 cc. of concentrated sulfuric acid. The sulfuric acid acts as a dehydrating agent in this reaction. Now heat the mixture over a low flame until a temperature of 150 to 160 degrees is reached. Continue heating at this temperature for about one hour.

Then pour the liquid into a large beaker containing 160 cc. of hot water. Heat to boiling and stir vigorously until the odor of phenol can no longer be detected. If you have a mecanical stirrer, you can put it to use here.

Phenolphthalein is present in the mixture in crude form. You can check this by allowing a few drops from your stirring rod to fall into a solution of sodium carbonate. The characteristic pink color is obtained. But the experiment does not stop here. The purification and extraction must be carried out.

Allow the solution to cool thoroughly. Or if you wish, allow it to stand over night and continue the experiment the following day.

When cool, the solution is filtered and the precipitate containing the crude phenolphthalein is transferred to a large beaker containing 200 cc. of warm water in which 3 g. of sodium hydroxide are dissolved. Add about 1 g. of decolorizing charcoal to the solution and heat for about five minutes (not to boiling) and filter again while hot. The filtrate should be colored a brilliant red hue, due of course to the presence of phenolphthalein. As you have deduced, phenolphthalein is insoluble in water, but soluble in sodium hydroxide solution.

In order to obtain the phenolphthalein, it will be necessary to acidify the solution. Cool the filtrate to about 20 degrees. Then add hydrochloric acid until the red color disappears and a heavy yellowish precipitate forms. Filter off the yellow solid and wash with water. Now the phenolphthalein which you purchase commercially is a white powder, whereas your product is yellow. This is simply a matter of further purification, and if you desire a white product, proceed as follows:

Dissolve the yellow powder in 25 cc. of ethyl alcohol; add 1 g. of decolorizing charcoal and heat (not to boiling) for a few minutes. Stir vigorously; allow to stand a few moments, then filter. Next pour the filtered alcohol solution in small quantities into a beaker partly filled with boiling water. Stir thoroughly after each addition. Allow the solution to cool and add a few cc. of hydrochloric acid to precipitate the phenolphthalein and filter to collect the precipitate. If the product is still yellow, the above procedure is repeated. Sometimes a faint yellow color persists and it is rather difficult to obtain a pure white powder.

Synthetic Perfumes and Flavorings

➤ AND NOW we come to a pleasant aspect of synthetic organic chemistry —perfumes and flavorings. The preparation of pleasant-smelling compounds is always a joy for the home chemist if for no other reason than to prove to friends that *good* smells as well as bad emanate from the chemistry lab.

Since the earliest times, fragrant essential oils were extracted from plants for use in perfumes and essences. Although this is still a large industry today, the synthetic products created by the organic chemist are being produced more all the time and it is possible that before long the natural products will be almost entirely replaced by the synthetic.

The first important synthesis in this field was that of coumarin, produced by Perkin in 1868. (You will recall, Perkin also prepared the first synthetic dye). This was followed some years later by the preparation of vanillin, which occurs naturally in vanilla pods, by Tiemann and Haarmann. The very expensive musk perfume obtained from the glands of the musk-deer has been made very cheaply in the laboratory. Here the *odor* is duplicated, although the compound is not entirely the same. Hence we have an "artificial musk" synthetic perfume.

The odor of violets can be obtained from citral, a component of lemon oil. The hawthorne blossom is duplicated from anisaldehyde; the heliotrope from piperonal; the rose from phenylethyl alcohol; lilacs from terpineol.

Most of the synthetic substitutes are considerably cheaper than the originals, making perfume available to everyone nowadays. We owe a vote of thanks to the organic chemist for allowing our girls to smell so sweet!

Wintergreen

➤ THE PLEASANT refreshing odor of wintergreen is one of the easiest to produce in the home lab. Oil of wintergreen is methyl salicylate and is made by heating together salicylic acid, methyl alcohol and sulfuric acid. Simply place the ingredients in a test tube and apply gentle heat. If you would like to prepare the oil in greater quantity, place 17 grams of salicylic acid in a flask and add 30 cc. of methyl alcohol. Then slowly add 5 cc. of concentrated sulfuric acid, with constant stirring. The flask is then heated

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gently (preferably on a steam bath, if available) with a reflux condenser attached for about 3 hours. If the condenser is not available, you can substitute a long glass tube and one-hole stopper. The tube should extend upward from the flask from 24 to 30 inches. After heating for this time, the oil forms in the bottom of the flask. Carefully remove as much of the upper layer as possible by decantation, or with a medicine dropper. Transfer the remaining liquid to a separatory funnel and add 30 cc. of water. Shake and draw off the lower layer, which is methyl salicylate.

Methyl salicylate is used widely as a flavoring material and also as a liniment to afford relief in muscular soreness and rheumatism.

Bananas

➤ In the section on "Esterfication" we described the preparation of ethyl acetate, which, as you probably noticed, has an odor somewhat similar to bananas. However, the compound commercially known as "banana oil" is usually iso-amyl acetate. You can prepare it by mixing together in an evaporating dish or small beaker, 5 cc. of iso-amyl alcohol, 2 cc. of glacial acetic acid and 3 cc. of concentrated sulfuric acid. Stir and smell cautiously. If you cannot detect an odor, heat the mixture *gently* and pour into about 100 cc. of water in a beaker. You will probably find the odor is actually more noticeable, and less penetrating, when the compound is mixed with the water.

Butyl acetate also has an odor of bananas. Repeat the above experiment using butyl alcohol instead of the amyl variety.

Finally, repeat the experiment using ethyl alcohol. Which acetate do you think smells most like bananas?

Pineapples

➤ The compound, *ethyl butyrate,* has the odor of pineapples and is prepared by heating together ethyl alcohol, butyric acid, and sulfuric acid. If you do not have butyric acid, it can be extracted from butter in which it occurs combined with glycerin (as glyceryl butyrate).

Place one teaspoonful of butter in an evaporating dish and heat gently until melted. Now weigh out approximately one gram of potassium carbonate and add it in small portions to the melted butter. It is necessary to stir constantly with a glass rod. Keep your face away from the mixture while heating as the fumes may be somewhat irritating. After the potash has been added, continue to heat the butter to boiling for several minutes. This process is known as *saponification.* Our chief concern with butter here is the glyceryl butyrate content, which we are attempting to extract in the form of potassium butyrate. Most butters contain about two per cent of glyceryl butyrate.

Our next step is to acidify the butter mixture. After it has boiled for a few minutes, remove it from the flame and add a small quantity of dilute sulfuric acid, stirring constantly. Keep adding the acid in small quantities until reaction ceases, which will indi-

cate the solution is acid. The solution should now be distilled. This can most conveniently be done with two test tubes. Pour the butter mixture into one of the tubes, and place a one-hole stopper in it containing a glass tube extending into a second test tube which is immersed in a tumbler of cold water. Heat the butter mixture gently until one-half the mixture distils over. The distillate should now contain a solution of butyric acid. By adding sulfuric acid to the butyrate salt, butyric acid, being more volatile is set free. It boils at 162°, and condenses in the cool distillate tube. Butyric acid has an unpleasant odor simi-

lar to rancid butter. ($CH_3.CH_2.CH_2.CO.NH_2.$).
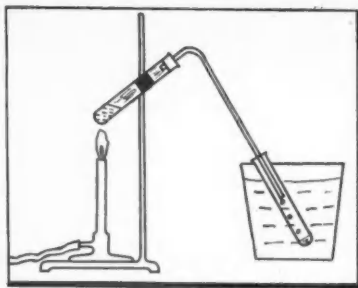
Now add a few cc. of ethyl alcohol to the distillate and an equal quantity of concentrated sulfuric acid, and distil the mixture once more, being careful not to heat the liquid too strongly. The distillate will contain an appreciable quantity of essence of pineapple which can be easily detected by its odor. It is a welcome product after working with the rancid odor of butyric acid.

Chemically, essence of pineapple is known as ethyl butyrate: $CH_3.CH_2.CH_2.COOC_2H_5$. Pure ethyl butyrate is a colorless liquid boiling at 120° with a specific gravity of 0.879. It is soluble in about 150 parts of water, and is miscible with alcohol, which solution is known as artificial "oil of pineapple".

Now if laughing friends deride, when acrid smoke gets in their eyes, you can take the pineapple oil from the shelf, and prove to them yourself, that the versatile chemist can create sweet soothing savors as well as evil-smelling vapors!

Apples

▶ ETHYL iso-valerate is the compound with an apple-like odor. It is prepared in the home lab by the action of iso-valeric acid with ethyl alcohol. Assuming the valeric acid is not normally on hand in the home, we will prepare it also. You will recall that we prepared acetic acid by the oxidation of ethyl alcohol; formic acid by the oxidation of methyl alcohol and benzoic acid by the oxidation of benzyl alcohol. In a similar manner we can prepare isovaleric acid by the oxi-

dation of isoamyl alcohol using chromic acid as our oxidizing agent.

Place 10 cc. of water in a flask and carefully add an equal quantity of concentrated sulfuric acid. Stir, then add 7 grams of potassium dichromate, and stir again until the solid has entirely dissolved. You now have a solution of chromic acid which is a powerful oxidizing agent. To this solution a total of 3 cc. of isoamyl alcohol is added *drop by drop*. The action is quite vigorous, so be careful

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not to add the alcohol too quickly. Shake the flask after each addition. The flask will become quite warm and the solution turns green. You will also probably notice an unpleasant odor somewhat like rancid cheese. This is due to valeric acid.

After all the alcohol has been added, heat gently for about ten minutes. You had better have adequate ventilation, as the smell is really putrid! Perhaps you are wondering how we get the fragrance of apples from this mess. Well, have patience!

Stir the mixture thoroughly and pour 5 cc. of it into a large test tube and add to it 5 cc. of ethyl alcohol. Now the mixture is distilled. This is most easily done by inserting a one-hole stopper in the test tube with glass tubing extending into another test tube immersed in cold water. (See illustration accompanying the preceding experiment on "Pineapples"). Heat the mixture gently and evenly until a small portion distills over. Carefully smell the distillate. Can you detect the apples?

Cinnamon

> IN THE SOUTH SEA islands of the Pacific, in Asia, and in Ceylon, there grows a plant which yields valuable volatile oils, and which is known scientifically as *Cinnamomum zeylanicum,* or more commonly as cinnamon. The household spice is obtained from the dried bark of this plant which sometimes attains a height of twenty feet. Also, from the bark, leaves and twigs of the plant, there is derived an oil which is used in medicine and as a flavor in foods and in the manufacture of perfumes. But it is no longer necessary to travel to the South Sea Islands to obtain this delightful, tangy flavor, for the practical chemist has created a method of preparing the oil in his own laboratory. Having analyzed the natural oil as a mixture of aldehydes, acetates, acids and alcohols, he found it possible to synthesize the chief ingredient of the oil—*cinnamaldehyde,* which possesses a pleasant cinnamon odor. It can for most purposes be used as a substitute for the natural oil.

Cinnamaldehyde is formed by the action of dilute alkali solution on a mixture of acetaldehyde and benzaldehyde. This is an example of a *condensation* reaction, where two substances combine to form a third one with the resultant elimination of water:

$$C_6H_5CHO + CH_3CHO \rightarrow$$
$$C_6H_5CH=CHCHO + H_2O$$
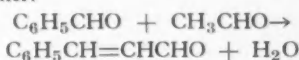
The dilute alkali acts as the *condensing agent.*

Mix together in a large test tube 5 cc. of acetaldehyde and 5 cc. of benzaldehyde and add 4 cc. of dilute sodium hydroxide solution. Stopper tightly and shake thoroughly for three or four minutes. Then immerse the tube in a solution of cold water, preferably ice water. Continue to shake the mixture occasionally from time to time. Remember, in organic chemistry patience is a virtue. Since organic compounds do not form ions they are slow to react. After about an hour of the ice water treatment, allow the stoppered tube to stand in a cool place for at least twelve hours. At the

end of this time a yellowish oily liquid will have formed in the test tube. Separate the oil by means of a separatory funnel or medicine dropper. Do you recognize the spicy odor?

While this experiment may appear relatively simple to perform, you may encounter some difficulty in obtaining the desired product. If such is the case, it may be that the component reagents used were not sufficiently pure. Therefore it is advisable to distil the acetaldehyde and benzaldehyde separately before using them in the experiment. Because of its flammability and low boiling point, care must be exercised in the distillation of acetaldehyde. Place small quantities at a time in a flask which should be immersed in boiling water. Do not heat the flask with a direct flame. When distilling benzaldehyde, add several pieces of clay plate or glass beads to prevent spurting and irregular boiling. Use both reagents immediately after distilling.

Hyacinth

➤ Many compounds can be prepared in the laboratory which duplicate the fragrance of popular flowers and the chemist utilizes these compounds as the basis for synthetic perfumes. One such compound is phenylacetaldehyde which possesses the delightful odor of hyacinths. It is made from cinnamic acid by treatment with hypochlorous acid and dilute sulfuric acid.

Our first step, then, is to prepare cinnamic acid. The famous chemist, Perkin, devised a method of synthesizing the compound by heating together sodium acetate, benzaldehyde, and acetic anhydride. We shall do likewise. Place 2 grams of *dry* potassium acetate in a flask. (It has been found that a better yield is obtained more quickly by using potassium acetate in place of the sodium salt.) Ordinary crystalline potassium acetate can be dried by heating gently in an evaporating dish with occasional stirring until all vapor is driven off and the salt is completely fluid. Allow the mass to solidify, grind to a powder in a mortar, and use immediately. Add to the potassium acetate in the flask

5 cc. of acetic anhydride and 3 cc. of *freshly distilled* benzaldehyde. (When distilling benzaldehyde, add small pieces of clay plate or glass beads to prevent bumping.) Mix the ingredients thoroughly and heat the flask allowing the solution to boil gently for at least a half-hour. If irritating vapors bother you, do not become discouraged. Open a window and carry on! At the end of the designated time, remove the flame and add 10 cc. of hot water to the contents of the flask. Add cautiously; the action may be somewhat vigorous. The mixture should now be steam-distilled until all unchanged benzaldehyde is removed (see below). However, if you do not have the facilities for doing this, it may be eliminated. Merely heat the solution to boiling again for 10 or 15 minutes. Then filter the hot solution quickly and heat the filtrate again to boiling and add a few cc. of hydrochloric acid. Allow the solution to cool, stirring occasionally. Cinnamic acid will crystallize out. Remove the crystals by filtering and redissolving in hot water. Cool and recrystallize.

Repeat this operation several times to obtain a purer product.

In describing this experiment we are taking into consideration the limited facilities of a home laboratory. Naturally, a 100% prue product can not be expected. Much better results can be obtained by using an air-cooled reflux condenser, heating the flask in an oil bath, steam distilling, and filtering with suction. But if such set-ups are not available, the home-chemist must not assume an attitude of discouragement; he must improvise.

Stir about $\frac{1}{2}$ teaspoonful of bleaching powder (chloride of lime) in 50 cc. of water. Allow the solid matter to settle, and pour off the clear solution. Prepare a solution of cinnamic acid by adding a small amount of the acid to 10 cc. of hot water. Heat further, if necessary, to dissolve as much as possible. Add to this an equal amount of the clear bleaching-powder solution. The reaction produces a compound known as phenyl-a-chloro lactic acid:—C_6H_5 . CH : CH . COOH $+$ HOCl $\rightarrow$ C_6H_5 . CH-OH . CHCl . COOH. Add a small quantity of dilute sulfuric acid to the mixture and heat gently. The result: phenylacetaldehyde: — C_6H_5 . CH-OH . CHCl . COOH $\rightarrow$ C_6H_5 . CH_2 CHO $+$ HCl $+$ CO_2. But what's in a name? ... that which we call hyacinth, by any other name would smell as sweet....

The Perkin synthesis of cinnamic acid is another example of a *condensation* reaction, similar to the preparation of cinnamaldehyde, as described previously. But whether the actual condensation takes place with the acetic anhydride is a matter open to
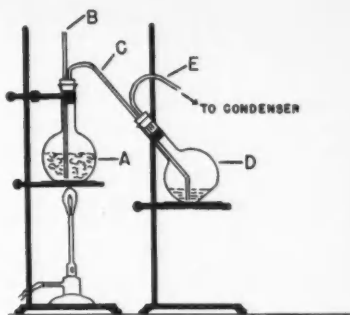
Steam Distillation

question. And just how much our patient reader is concerned with how the condensation takes place is also a matter open to question!

Steam Distillation

In many organic experiments, it is desirable to purify compounds by steam distillation. A simple method of doing this is shown in the accompanying diagram. Steam is generated in flask A by heating water and is conveyed via tube C into the liquid to be distilled in flask D. Tube B, extending almost to the bottom of the steam-generating flask, acts as a safety valve. The distillate passes through tube E which leads to a condenser or to a flask immersed in cold water (not shown). Make sure all connections are tight. It may be necessary to heat flask D gently to prevent too much condensation. When distillation is completed, disconnect tube C *before* removing heat from flask A; otherwise contents of flask D may be sucked back into the generator.

Orange Blossoms

➤ THE ETHYL ester of beta-naphthol, ethyl beta-naphtholate, has a pleasant odor similar to orange blossoms. It is prepared by heating gently together in a test tube a mixture of 2 cc. ethyl alcohol, ½ gram beta-naphthol and about 10 drops of concentrated sulfuric acid.

The methyl ester also has a pleasant odor. To prepare it, proceed as above substituting methyl alcohol in place of the ethyl.

Coumarin

➤ THE SYNTHESIS of coumarin presents a challenge to the home chemist. It is prepared by a reaction known as the *Perkin Condensation.* The Perkin reaction, named after its originator, consists of heating together the salts of certain acids with a suitable aromatic aldehyde and the anhydride of the appropriate acid. Thus, cinnamic acid can be prepared by heating benzaldehyde with acetic anhydride and sodium acetate. With sodium propionate and propionic anhydride, *a*-methylcinnamic acid is obtained. Heating together salicylaldehyde, acetic anhydride, the sodium acetate will produce coumarin.

For best results, special equipment should be used to perform this experiment. This makes it a little difficult to carry out in a home laboratory. But, perhaps you can borrow some equipment from a school or commercial laboratory.

We used a round bottom, short neck boiling flask with a thermometer well and Ts glass joint. Capacity: 200 ml. Joint size: $2\frac{4}{40}$. Brand: "Pyrex" — Corning Nos. 4323 and 4324. With this flask was used a Liebig-type condenser with Ts joint at the bottom which fits snugly in the top of the flask. ("Pyrex" brand, Corning No. 2360.) Thus no cork or rubber stoppers are needed. The test tube fused in the side of the flask is used to hold a thermometer. Fill this tube partially with paraffin oil. The oil acts as a heat-transfer agent and its temperature will represent the temperature of the liquid inside the flask.

The condenser is inserted in an upright position and cooled by running water through it. This arrangement will allow us to boil the reaction for a long period of time without evaporation.

Before you begin, make sure all equipment is thoroughly clean and dry. After washing, rinse all vessels with alcohol and then with petroleum ether. Wait a few minutes for the solvent to evaporate completely and the equipment will be ready for use.

Place in the flask 32 grams of *anhydrous* sodium acetate and ½ gram of iodine crystals. (The anhydrous sodium acetate can be prepared from the crystalline variety by heating gently in an evaporating dish until all water is driven off. Stir constantly, and pulverize the product in a mortar.) Next, pour 18 cc. of salicyaldehyde and 30 cc. of acetic anhydride (*carefully!*) into the flask.

Insert the reflux condenser in the flask and a thermometer in the paraffin oil which is in the side tube. Apply heat until a temperature of 120 degrees is reached and continue heating at this temperature for two hours. Then increase the temperature to 180 degrees and hold as near as possible to this temperature for an additional five hours. If necessary, you may discontinue the reaction, stopper the vessels, and continue heating at another time. The most difficult part of the experiment is to hold a constant temperature over such a long period of time.

After the heating is completed, allow the contents to cool somewhat and pour into about 50 cc. of water,

stirring rapidly. Of course, keep your face away to avoid any splattering. The coumarin is present in this liquid. To separate it, we must extract with ether in which it is very soluble. Pour in 30 cc. of ether and stir thoroughly for about 5 minutes. Allow the mixture to stand and then carefully pour off the ether (top) layer. Be very careful when working with ether. Remember it is highly flammable and its vapor mixed with air is explosive. Use adequate ventilation and keep away from all open flames.

No doubt there will be some unreacted salicyaldehyde present. To remove it, shake the ether solution with a concentrated solution of sodium bisulfite. Again, allow the mixture to stand and pour off the top ether layer. Next, "wash" the ether by adding water, shaking thoroughly and again pouring off the top layer as before. Finally, pour the ether solution in a shallow dish and allow it to evaporate. Do not apply heat! The residue is crude coumarin.

Coumarin occurs in the Tonka bean, woodruff, and sweet clover. It is partly responsible for the refreshing odor of new-mown hay. Coumarin itself has a pleasant odor similar to that of the vanilla bean, which in great dilution resembles new-mown hay. It is used in perfumery and as a flavoring agent.

Dissolve a small particle of coumarin in ethyl alcohol. Does the odor remind you of vanilla extract?

Synthetic Plastics

➤ In RECENT years, synthetic plastics have become more useful and more popular. The public apathy, which first considered plastics as "cheap substitutes", has been overcome with the advent of much improved products.

The oldest synthetic plastic is that made of *pyroxylin,* a form of cellulose nitrate. Pyroxylin containing camphor as a plasticizer appeared in England in 1877 under the name "Xylonite". A similar product was manufactured in this country known as "celluloid". Celluloid has been widely used for many years, but, because of its high flammable nature, it is rapidly being replaced by the newer plastics.

"Bakelite" was the first of the phenol-formaldehyde resins to be produced commercially (1909). Other similar plastics have been made from furfural-phenol and urea-formaldehyde combinations.

More recently the plastics have been made from phthalic anhydride and glycerols (the "alkyd resins"). Another group, the "vinyl resins", is produced from the polymers of vinyl acetate and vinyl chloride.

Still another important plastic, "polystyrene", has been known since 1839 but was not produced successfully until 1937. It is formed by the polymerization of styrene which is produced from ethylene and benzene.

The plastic and resin industries are ever expanding as new and better products are being produced. It is becoming more difficult to keep abreast of the products. For what we report as the latest product today is outdated tomorrow by a newer version.

Bakelite

➤ No DOUBT many chemists in the past during the course of their research, have mixed together the two common compounds, phenol and formaldehyde. And no doubt they encountered the sticky, tacky mass formed by heating the two chemicals, which rapidly hardens to a brittle mass that could neither be crystallized, dissolved, distilled, nor analyzed. Disgusted, they attempted the difficult task of cleaning their glassware and considered the experiment a failure. In the future they would carefully avoid the preparation of this troublesome resin.

But one chemist repeated the experiment and did not throw the stuff

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away. Dr. Leo Hendrik Baekeland had vision; instead of discarding the substance, he paused and considered. (Incidentally, to pause and consider occasionally is a commendable act which we highly recommend to all home chemists.) Why couldn't it be put to some valuable use? Maybe it would serve as a plastic?

Perhaps.

Preparation

Bakelite is not too difficult to prepare in the home laboratory. Place 3 grams of phenol (carbolic acid) in a small flask. Add 6 cc. of formaldehyde (37%) and 10 drops of sodium hydroxide solution. Apply an even, moderate heat. The liquid will change to a red color and will gradually become more viscous. Continue heating until the mixture attains a thick, molasses-like consistency. Remove from the flame and quickly pour into a test tube, which will serve as a mold. If you wish you may use a crucible, watch glass, or similar container for this purpose. The liquid will gradually harden to a thick, gummy mass,

The next step is the process of baking, which forms the hard familiar type of bakelite. The baking requires prolonged heating at a temperature of 60 to 75 degrees C. At least three hours are required, preferably more. You may use your own ingenuity in carrying out this process. You can build an "oven" from a tin can and suspend the test tube in it, heating the can with a small flame; or you can use an electric light bulb to supply the heat. The important thing is to maintain a nearly constant temperature for a long period of time.

It may be necessary to break the tube in order to obtain the bakelite in a solid piece. The substance may be somewhat brittle, but in most respects will resemble the commercial product.

Technicality

What actually happens when phenol and formaldehyde are blended together? The resinous substance is formed by the process of *polymerization,* which refers to molecules combining with themselves to form a larger molecule, known as a *polymer.* Bakelite is a synthetic polymer. In this type of reaction, o and p-hydroxybenzyl alcohols are formed, which molecules condense to form networks of molecules. To these molecules are linked the methylene radicals. This process continues, building larger and larger groups of molecules until the final resin is formed. The sodium hydroxide acts as a catalyst.

The chemical name for bakelite is oxybenzylmethyleneglycolanhydride. It belongs to the group of plastics known as *thermosetting* resins. These resins, once molded, are permanently hard and cannot be re-molded. The *thermoplastic* resins, such as the cellulose derivatives and the newer vinyl plastics, can easily be re-molded under the influence of heat and pressure.

Usefulness

Thus from the observation of Baekeland has grown the giant Bakelite Industry. Bakelite is widely used in the insulating of many electrical devices, in the manufacture of radio cabinets, telephone receivers and transmitters, push buttons, switch blocks, billiard balls, brush handles, combs, pens, pencils, and hundreds of similar articles.

All from the sticky, gummy sub-
stance which could neither be crystal-
lized, dissolved, distilled, nor ana-
lyzed.

But one chemist had vision.

He did not throw the stuff away.

Urea Synthesis

➤ ONCE UPON A TIME the science of
chemistry consisted of two separate
divisions: inorganic chemistry — the
study of materials derived from the
mineral kingdom, and organic chem-
istry — the study of materials derived
from living organisms. Then it was
the opinion of leading chemists — in-
cluding the famous Berzelius — that
organic compounds could be formed
only through the function of a living
organism. Therefore the preparation
of any organic compound in the lab-
oratory without this "vital force" was
absolutely impossible.

But the impossible happened! In
1828, Wöhler heated a solution of am-
monium cyanate — an inorganic com-
pound — to dryness. Upon examina-
tion of the residue, he found that it
contained urea — an organic com-
pound! This couldn't be! It was
against all theories then in existence!
Very doubtful of his results, Wöhler
repeated the experiment many times
before he finally believed that this
transformation actually took place.

"I must tell you," he wrote to
Berzelius, "that I can prepare urea
without requiring a kidney or an
animal, either man or dog."

As happened in the past and prob-
ably will happen in the future, the
most elaborate theories are crushed by
a simple experimental fact.

The preparation of urea by Wöhler
was of important historic significance
because it was the first time an organ-
ic compound had been prepared syn-
thetically in the laboratory. If Wöh-
ler and Berzelius were amazed at this
synthesis, how would they feel if they
could view the thousands of com-
pounds made synthetically by the
chemist of today!

Preparation

You can repeat Wöhler's synthesis
of urea in the home lab without too
much difficulty. Because of its instabi-
lity, ammonium cyanate is prepared
by mixing solutions of potassium
cyanate and ammonium sulfate. Upon
evaporation, the ammonium cyanate
is converted into urea: $NH_4CNO \rightarrow NH_2CONH_2$, which is obtained as a
white powder mixed with potassium
sulfate. The urea is extracted with
alcohol, in which potassium sulfate is
insoluble.

Dissolve 3 grams of potassium cya-
nate in 15 cc. of water, and add an
equal quantity of ammonium sulfate.
After all solids are thoroughly dis-
solved, transfer to an evaporating dish
and heat to dryness, stirring frequent-
ly. Continue heating until the solid
residue is completely dry. Powder the
residue with a pestle, then add 5 or 10
cc. of absolute alcohol (either ethyl or
methyl). Heat the alcohol to boiling
on a steam bath for about 5 minutes;
then filter off the undissolved potas-
sium sulfate. Add to this another 5 or
10 cc. of alcohol and repeat the ex-
traction. Combine the two filtrates
and cool thoroughly by immersing the

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container in an ice-salt mixture. Crystals of urea will separate; filter them off, allow to dry (do not heat).

If potassium cyanate is not available, it can be prepared by the oxidation of potassium cyanide. Dissolve 2 grams of potassium cyanide (*extremely poisonous—handle with great care*) and 2 grams of sodium hydroxide in 35 cc. of water. Thoroughly pulverize 4 grams of potassium permanganate and add to the above solution in small quantities over a period of fifteen minutes. Stir the solution after each addition, but do not allow the temperature to rise above 60°. You might find it more convenient to use a thermometer as a stirring rod. After all the permanganate has been added, heat the mixture in a water bath at about 60° (not over) for about two hours. If necessary, add a small portion of dilute sodium bisulfite solution to use up any unreacted permanganate. Filter off the manganese dioxide, and wash several times with water. The filtrate, which should be colorless, contains potassium cyanate. Add to this 8 grams of ammonium sulfate and evaporate to dryness to obtain the urea described above.

Urea can also be prepared by heating carbon dioxide and ammonia under pressure or by decomposing calcium cyanamide with dilute sulfuric acid.

It is used in stablizing explosives, as a fertilizer, in the manufacture of plastics and in the synthesis of pharmaceutical compounds — chiefly barbital and allied products.

Save the urea you have prepared, and proceed to investigate its properties and related compounds.

Urea or carbamide, CH_4N_2O, con-sists of colorless or white crystals very soluble in water and melting at 132 degrees. It occurs in the blood and tissue fluids and is also present in urine to the extent of approximately 2%. It is excreted from the body as a waste product, or, more technically, as the end product of animal metabolism.

If for some reason you were unable to prepare urea, you can probably purchase a small quantity from the corner drugstore for these experiments.

Identification

(1) Dissolve a small quantity of urea in 1 cc. of ethyl alcohol. Dissolve an equal quantity of oxalic acid in an equal volume of ether. Mix the two solutions. The urea separates as a white crystalline precipitate.

(2) If a solution of sodium hypobromite be added to a solution of urea, a violent effervescence takes place with the evolution of nitrogen and carbon dioxide:

$$CH_4N_2O + 3\ NaOBr \rightarrow$$
$$CO_2 + 3\ NaBr + 2\ H_2O + N_2$$
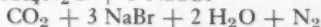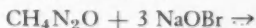
If sodium hypobromite is not available, a substitute reagent can be prepared by dissolving equal quantities of salt and potassium bromide in a dilute solution of sodium hypochlorite ("Clorox").

(3) Make a solution of urea alkaline by adding a small quantity of dilute sodium hydroxide. To this solution add a few drops of mercuric chloride solution. A white precipitate forms.

(4) To 5 cc. of a solution of urea, add 5 drops of HCl and 5 drops of formaldehyde. Mix gently. Nothing will happen at first; however if the

solution is allowed to stand for about 10 or 15 minutes, a white precipitate of diformaldehydeurea will suddenly form.

Since it is an amide, urea undergoes hydrolysis when warmed with alkali:

$$CH_4N_2O + 2\ KOH \rightarrow$$
$$2NH_3 + K_2CO_3.$$
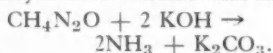
Place about $\frac{1}{2}$ gram of urea in a test tube. Add 5 cc. of sodium hydroxide solution and heat to boiling. You will soon be able to recognize the odor of ammonia, indicating hydrolysis.

Biuret

When urea is heated carefully, biuret (allophanic acid amide),

$$NH_2.CO.NH.CO.NH_2.H_2O,$$

is obtained. This compound is not particularly important. It is best known for its reaction with copper sulfate which is a popular test for proteins (the "biuret reaction").

Place a very small quantity (about 0.2 gm.) of urea in a dry test tube and apply gentle heat. The powder melts to a clear liquid with the production of ammonia. Continue to heat gently. After the ammonia is driven off, the liquid will turn milky and gradually solidify with the formation of biuret. Allow to cool, and add about 1 or 2 cc. of sodium hydroxide solution. Dissolve the solid thoroughly; then add a few drops of dilute copper sulfate solution. A lovely red-purple coloration is obtained. This reaction is characteristic of proteins and polypeptides. As the number of peptide linkages is increased, the color deepens; proteins usually produce a violet color.

Urea Nitrate — To a concentrated solution of urea, add a few drops of nitric acid. Immediately a crystalline precipitate is formed which settles quickly to the bottom of the tube. Urea nitrate will dissolve in an excess of water.

Urea Oxalate — Proceed as above using concentrated oxalic acid solution instead of nitric acid. Crystals of urea oxalate will separate out and fall through the liquid like a miniature snowstorm. This compound will also dissolve in excess of water.

Other compounds formed similarly are urea hydrochloride and urea phosphate. Urea also forms a number of additional compounds with inorganic salts, but they are not important.

Uses

Urea forms thermosetting resins with formaldehyde, similar to the phenolformaldehyde type. They are sold under the trade names of "Beetleware" and "Plaskon."

Dissolve 1 gram of urea in 8 cc. of water; add 2 cc. of hydrochloric acid and 2 cc. of formaldehyde. Shake thoroughly and allow to stand. The mixture will turn white and gradually harden.

New uses are still being found for urea — the first organic compound ever prepared synthetically. Perhaps you remember the recent stir about anti-decay tooth powder. Scentists discovered that brushing the teeth with a mixture of urea and dibasic ammonium phosphate is useful for the prevention of decay. It is the same product you have been experimenting with, but in toothpaste urea is marketed under its chemical name, carbamide. Thus a waste product of nature is used to prevent waste in the form of tooth decay!

Artificial Camphor

▶ THERE IS obtained from turpentine a white crystalline solid known as bornyl chloride. Because this substance has the appearance and odor of camphor, it has often been called "artificial camphor." It is not too important a compound in itself, but it is used as a starting point to prepare *synthetic* camphor. Now, you do not want to confuse the terms "artificial" and "synthetic." Artificial is an imitation of the real thing, whereas synthetic *is* the real thing. Thus we have *natural* camphor — which is as it is obtained from nature; *synthetic* camphor — the same substance made in the laboratory; *artificial* camphor — an entirely different substance that is similar to camphor.

Common turpentine consists chiefly of *a*-pinene ($C_{10}H_{16}$) along with a smaller percentage of β-pinene (nopinene). Pure *a*-pinene boils at 154-156 degrees and β-pinene at 163 degrees. As we need the *a*-pinene for our experiment, it should not be too difficult to obtain it from turpentine.

Obtain a good grade of steam-distilled wood turpentine from the paint store. Pour 10 cc. of it into a distilling flask and insert a thermometer into the liquid through a one-hole stopper.
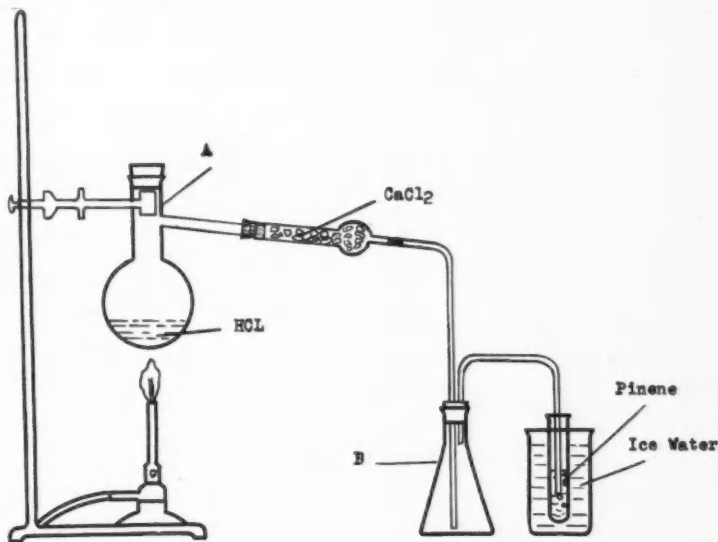
▶ THE PREPARATION *of bornyl chloride from a-Pinene*

Connect a tube to the side arm of the distilling flask leading into a test tube externally cooled by immersion in ice water.

Heat the flask gently and collect all of the liquid that distils over between 154 and 156 degrees. Distil about one-half of it (5 cc.). Be careful, as turpentine is flammable. Your distillate should be a fairly pure version of *a*-pinene.

To convert the *a*-pinene into bornyl chloride, it is necessary to saturate it with dry hydrogen chloride at a low temperature. In order to accomplish this, set up an apparatus as shown in the diagram. The flask 'A' contains 10 cc. of concentrated hydrochloric acid. The calcium chloride drying tube is attached to the side arm of the distilling flask 'A.' Flask 'B' is placed in the set-up to catch any excess moisture which may drain out of the drying tube. The test tube containing the 5 cc. of *a*-pinene is immersed in a container of ice water.

Heat the hydrochloric acid gently and allow the dry hydrogen chloride gas to bubble through the cool *a*-pinene until the latter is saturated. It is difficult to state just when this point is reached; you will have to use your own judgment here.

When dismantling the apparatus, disconnect flask 'B' first; then remove the flame. This will prevent any liquid from being sucked back into the flask.

Bornyl chloride is insoluble in water. Add water to the solution in the test tube, shake well and allow to stand. Note the white solid particles which separate from the solution. Does the odor remind you of camphor?

Synthetic Camphor

The synthesis of camphor is a bit involved for the home laboratory. However you may be interested in the method which uses bornyl chloride as the starting point. First it is converted into camphene by heating with potassium phenoxide at 180 degrees. The camphene thus obtained is treated with glacial acetic acid at 60 degrees to form isobornyl acetate. Then the isobornyl acetate is hydrolyzed to isoborneol by boiling with alcoholic potassium hydroxide. Finally, the isoborneol is converted into camphor by oxidation with fuming nitric acid. That's all there is to it. Some day when you feel ambitious, you can attempt the synthesis.

Artificial camphor has few commercial uses, but synthetic camphor is highly useful and is manufactured on a large scale. It is used in the manufacture of plastics (notably celluloid), lacquers, varnishes, explosives, in various pharmaceuticals and cosmetics, and, of course, as a moth repellent.

Synthetic Rubber

➤ DURING the years between the two wars the supply of natural rubber was more than ample, and the product was available cheaply and in abundance. Consequently little thought was given to any synthetic replacement. When the second war began, however, the supplies of natural rubber dwindled rapidly. If we were to continue our position in the war it

became necessary to find another source of the all-important rubber. It was up to the scientist to produce this source. And, as many times in the past, when the need for a particular item arose, science found a way to obtain it. It was not long before synthetic rubber was prepared in the laboratory and was followed shortly thereafter by industrial production.

Many types of synthetic rubber have been prepared and new combinations are being discovered constantly.

Synthetic rubber is produced through a process known as *polymerization,* which involves inter-molecular combinations. The *polymers* resulting from this reaction are of the elastic type, such as synthetic rubbers, and the non-elastic types, such as synthetic plastics. The rubber-type of compounds are known as *elastomers.* Actually, the elastomers do not duplicate natural rubber. They are separate products *similar* to natural rubber, and in many respects superior to the natural product.

Among the many types of rubber-like compounds are the butadiene rubbers, piperylene rubbers, isoprene rubbers, dimethylbutadiene rubbers, haloprene rubbers (such as neoprene), elastolenes (such as Butyl rubber) and elastothiomers (such as Thiokol). Of this group, Thiokol is perhaps the most easily adapted for home laboratory preparation. It is produced essentially from the reaction of sodium tetrasulfide with ethylene dichloride.

Dissolve 3 grams of sodium hydroxide in 60 cc. of water. Place the solution in a large beaker and heat to boiling. To the boiling liquid, add 6 grams of finely powdered sulfur. Add

small portions at a time, stirring constantly. After all has been added, continuing stirring and heating for a few minutes. Then, remove the heat, add about 50 cc. of water, stir, and filter off any unreacted sulfur. The resultant filtrate should be a clear red liquid (sodium polysulfide).

For an emulsifying agent, we will use a soap solution. Dissolve about one-half gram of soap flakes (such as "Lux" or "Ivory") in 10 cc. of hot water. Heat the sodium polysulfide solution prepared above in a large beaker to a temperature of 70 degrees, and add the soap solution to it. Next, while stirring, add 10 cc. of ethylene dichloride in small portions. It is important that you keep the temperature at 70 degrees. If it should rise, remove the heat immediately and if necessary cool the beaker externally. Continue stirring at the 70 degree temperature until the liquid becomes milky-white in color. The solution will pass through various shades of orange, yellow and ivory. But do not be satisfied until you obtain an entirely white color. This white emulsion is the "latex." Cool the solution and add 5 cc. of concentrated ammonium hydroxide, which will act as a stabilizer. Stir again and allow the mixture to stand for a day or two.

The latex emulsion will gradually settle to the bottom of the container. Carefully pour off the clear liquid from the top. Then add the white emulsion to 150 cc. of water in a beaker. Add 5 cc. of concentrated ammonium hydroxide and stir well.

Our final step is to coagulate the rubber. This can be done with dilute acetic acid (about a 20% solution). Add the acetic acid in small quantities

with continual stirring until the Thiokol separates out of solution as a lump in the bottom of the container. Remove the lump and wash it thoroughly with water. This is the crude synthetic rubber. Note that it is moderately elastic.

The elasticity can be increased by treatment with zinc oxide and carbon black. Place the lump of rubber in a mortar. Add about one-half gram of zinc oxide and a small pinch of carbon black. Work the chemicals into the rubber by kneading with the pestle. Do not grind — rather press the chemicals in. Note the elasticity after you have treated the rubber for about 15 minutes.

The procedure you have just completed is similar to that of processing natural rubber. The difference, of course, is that the milky latex is obtained from the rubber tree instead of from chemical reaction. The natural latex is also stabilized and then coagulated with acetic acid. This rubber is then vulcanized and further treated with carbon black or zinc oxide which help to increase its resiliency, strength, and toughness.

Natural rubber is a complex polymerized form of isoprene. The Thiokol that you have prepared is actually a "substitute" rubber. It is unaffected by hydrocarbons and most solvents. Thus it is used in making hoses used to handle such liquids.

So much for synthetic rubber. A life saver during times of war. A mighty important supplementary product during times of peace. Another triumph of chemistry!

Glass

Bouquets of orchids to the lad or lass,
Whoever it was, who first made glass . . .

▶ LIKE the wheel, glass is on of those substances known and used since the dawn of history. Archaeologists have unearthed objects made of glass which they claim were used by the Egyptians as early as 5000 B.C. It is remarkable that glass was prepared so long ago, when we consider that even today it is not the easiest product to manufacture. It is also remarkable that no major improvements were made in its manufacture until the present century. And only very recently have different types of glass been developed for diversified uses.

Glass may be considered a mixture of the silicates of certain metals, usually sodium, calcium or potassium. It is made by heating silica (ordinary sand) and sodium carbonate along with various other compounds depending upon the type of glass desired.

How to Prepare

There are several different methods to prepare crude glass in the laboratory. In all cases you should have a good source of heat. If a Bunsen burner is not available, perhaps you can take advantage of the gas flame on the kitchen stove. Use an old porcelain crucible for this reaction, as you will probably have to break it in order to remove the glass. Mix to-

gether thoroughly, by grinding in a mortar, one ʼram of powdered silica (fine, clean sand), one gram of powdered sodium carbonate and two grams of yellow lead oxide (litharge). Transfer the mixture to the crucible. Apply heat, gradually increasing until the mixture melts. Scrape off the scum from the molten mass with a glass rod and allow the crucible to cool. The glass hardens, forming a hard brittle layer on the bottom of the crucible. Do not expct your glass to be transparent. Very pure ingredients must be used in order to produce clear glass. If you prefer a blue colored glass, add a small crystal of cobalt nitrate to the above mixture before heating. Add also a few drops of water to form a heavy paste. Then proceed as outlined.

If you do not wish to sacrifice a crucible for this experiment, you can try using a *hard* glass test tube instead.

Glass Bead

Another method to prepare glass is by using a wire. Take the wire, preferably platinum, and make a small loop in the end of it. Using a pliers, heat the wire in a gas flame. Then dip the hot wire into some powdered sodium carbonate. Heat the chemical in the flame until a clear bead is formed. Next take up some powdered silica with the hot bead and heat until the two compounds are fused together. Finally, dip the hot bead in powdered calcium carbonate and heat once more. You will end up with a small bead of glass.

Is glass soluble in water? Grind a small piece of glass to a fine powder in a mortar. Be sure to protect your eyes during this operation. Add a few

drops of water and a drop of phenolphthalein solution. Note the pink color, which indicates a small portion of the glass has dissolved.

Flint Glass

The first glass we have made is a type of *flint* glass. In a more refined form it is used to make lenses and cut glass dishes.

The glass we made on the wire is ordinary window or bottle glass. It is called soda-lime or "soft" glass, because it is easily softened by heat.

"Hard" glass, with a higher melting point, is made by substituting potassium carbonate for the sodium compound. This glass is used in making laboratory glassware.

"Pyrex" glass contains compounds of boron in addition to the sand and soda. This type of glass (borosilicate glass) has a small coefficient of expansion and finds considerable use in the laboratory and in the kitchen.

Safety glass, used in automobiles, is made by placing sheets of plastic resin between two plates of glass and heating under pressure.

Colored glass is made by adding various chemicals to the batches. For example, selenium produces red glass, manganese forms violet glass, and chromium or copper produce green glass.

Newer uses of glass include glass bricks used for construction, and spun glass woven into fabrics.

Pure silica can be melted (about 1700 deg. C.) to form quartz glass. This glass does not crack under sudden temperature changes. You can heat a vessel made of quartz glass to white heat then plunge it into cold water without breaking. It is also

transparent to ultraviolet light, which ordinary glass is not.

One of the newest types of glass is sold under the name "Vycor." It resembles the quartz glass, but costs considerably less to produce. It is made from borosilicate glass. The borosilicate is treated with nitric acid, which removes most of the constituents except the silica. The remaining silica is subjected to heat treatment to obtain the finished product, which is actually 96% pure silica.

We certainly need not stress the importance and usefulness of glass. For over 6000 years it has stood alone as an irreplaceable product. Only very recently has it had any competition of any sort—that of the transparent plastics. Nevertheless, we feel that glass will still be around for a good many years!

Paint

► ORDINARY PAINT consists of two general components: the *pigment,* which contains the coloring matter, and the *vehicle,* an oil in which the pigment is suspended. Of course, various other substances are added to obtain specific properties. Sometimes a *filler* (such as silica, kaolin, barium sulfate, or calcium carbonate) is added to give greater bulk and decrease the cost. A *drier* is added to hasten the drying process. The substance is usually the water-insoluble soap of cobalt, manganese or lead. Finally, a *thinner* must be included to obtain proper consistency for easier application.

Most manufacturers list the essential ingredients of their paint on the label. For example, we found a can of exterior green house paint in the cellar with the following analysis:

Pigment 37.7%:-
    Chrome Green   - - - 75.0%
    Magnesium Silicate - - 25.0%
Vehicle 62.3%:-
    Linseed Alkyd Resin - 50.0%
    Driers - - - - - - 1.7%
    Mineral Spirits   - - 48.3%
This paint was further tinted with chrome yellow and titanium dioxide to obtain the desired shade.

A can of inside semi-gloss white enamel had the following composition:

Pigment 51%:-
    Titanium Oxide - - - - 51%
    Calcium Carbonate - - - 41%
    Silicates - - - - - - 3%
    Zinc Oxide - - - - 5%
Vehicle 49%:-
    Soya/Linseed Alk. Resin - 43%
    Drier - - - - - - 5%
    Aliphatic Hydrocarbons - 52%
And, finally, an exterior White Lead paint:

Pigment 72.2%:-
    Basic Lead Carbonate - - 100%
Vehicle 27.8%:-
    Linseed Oil - - - - - 72%
    Mineral Spirits - - - - 23%
    Liquid Drier - - - - 5%

Note that the green paint employs magnesium silicate as the filler or "body," while the inside enamel uses calcium carbonate and the white lead paint contains only one compound which acts as coloring matter, filler and body. The vehicle in all cases is linseed oil or the newer linseed alkyd

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resins. The latter consist of alkyd resins (such as those made from glycerol and phthalic anhydride) modified with linoleic acid, which is present in linseed oil as a glyceride. They tend to make a rapid-drying paint with a durable finish. The thinner in most modern paints is usually a petroleum fractionation product, such as mineral spirits, or, in some cases, an odorless aliphatic hydrocarbon.

You can make a small quantity of paint in the laboratory by grinding together the pigment (see below) with linseed oil to form a smooth, syrupy paste. The most difficult part will be to obtain a really smooth mixture free of small particles. The product is then diluted with turpentine to the desired consistency.

The pigment is prepared by mixing together the proper solutions and filtering off the resultant precipitate. The precipitate is scraped off, transferred to a metal or glass container, and carefully dried over gentle heat. In the following descriptions, the compounds are simply designated as "solutions." The strength of these solutions is entirely up to you and depends on how much pigment you care to prepare. Usually one gram in 10 cc. of water makes an average strength solution. Be sure all solids are thoroughly dissolved before mixing the solutions. Use heat if necessary.

Yellow:

Mix sodium dichromate solution with an equal quantity of lead acetate solution. This is *chrome yellow*.

Another yellow pigment — "orpiment" — can be made by passing a stream of hydrogen sulfide gas through a solution of arsenious acid (*careful—very poisonous*) to which a few drops of hydrochloric acid have been added.

Blue:

A solution of ferric chloride is mixed with a solution of potassium ferrocyanide. The deep blue pigment is known as "Prussian Blue."

If you prefer a lighter shade of blue, add ferrous sulfate solution to the potassium ferrocyanide. This pigment is commonly called "Turnbull's Blue."

Green:

We learned in school that yellow plus blue equals green. Hence to obtain a green color we shall mix Chrome Yellow with Prussian Blue. Mix together a solution of sodium dichromate with a solution of ferric chloride. In another vessel mix together solutions of lead acetate and potassium ferrocyanide. Finally, combine the two mixtures. This pigment is sometimes sold as "chrome green."

Actually, chrome green pigment is pure chrome oxide prepared by igniting ammonium bichromate. Heat the compound in a dry metal pan. The crystals will suddenly flare up and chomic oxide is formed in the midst of a sparkling pyrotechnic display. (Keep your face away!).

Orange:

"Chrome orange" pigment is prepared by mixing together solutions of sodium dichromate and sodium hydroxide, and then adding a solution of lead acetate.

Red:

Vermilion is a brilliant red pigment. It is mercuric sulfide and is prepared by bubbling hydrogen sulfide

into a solution of mercuric chloride. The resultant black precipitate is filtered off and heated until it turns red.

Iron oxide forms a reddish-brown pigment. Mix together solutions of ferric chloride and ammonium hydroxide.

White Lead:

This popular white pigment can be made in the laboratory by mixing a solution of lead acetate with a smaller quantity of sodium carbonate solution.

Of course these are only a very few of the many pigments available. In addition to these are many "tinting" pigments which are used with white pigments to obtain various shades of ivory, cream, grey, etc. Some examples are:

Lampblack—carbon.

Raw Umber—Hydrated ferric oxide with manganese dioxide.

Burnt Umber—Calcined raw umber.

Raw Sienna—Hydrated ferric oxide with a smaller quantity of manganese dioxide.

Burnt Sienna—Calcined raw sienna.

As in other chemical industries, the paint industry is constantly changing and improving. Instead of the former white-lead linseed oil turpentine type of paint we now have the titanium dioxide-soya alkyd resin-aliphatic hydrocarbon type. This is just another example of the almost routine role that chemistry is constantly playing to improve the products we use.

$\bigstar \quad \bigstar \quad \bigstar \quad \bigstar \quad \bigstar \quad \bigstar$

Common Inorganic Elements

> IN THE various organic reactions we have described the introduction of inorganic elements into organic compounds, such as hydrogen, oxygen, nitrogen, chlorine, bromine, iodine, fluorine and sulfur. Since these elements play such an important role in organic chemistry, it might be a good idea to explore their properties individually. Although not strictly "organic" chemistry, we feel you will enjoy learning about these interesting elements in their own environment.

Oxygen

> ALTHOUGH oxygen comprises only 21% of the air, it is by far the most active component. Of course, it is essential to life. It combines with most other substances at elevated temperatures, accompanied by flame. We call this procedure "combustion" and oxygen a "supporter of combustion." Naturally, if a substance burns readily in air, you can imagine how much more rapidly it will burn in pure oxygen. This can be demonstrated in the home laboratory in an exciting display of pyrotechnics.

It is rather difficult to obtain oxygen in a pure state from the atmosphere. Thus we will obtain it from compounds. Potassium chlorate, for instance, contains oxygen which is readily released by heating: $2KClO_3 \rightarrow 2KCl + 3O_2$. If we should add manganese dioxide, the oxygen is liberated at a much lower temperature. The manganese dioxide, merely acts as a *catalyst* in this reaction and

remains unchanged. In some manner, not clearly understood, it forces the potassium chlorate to release its oxygen faster.

Mix together thoroughly and carefully 5 grams of potassium chlorate with 2 grams of manganese dioxide. Mix the chemicals on a clean piece of paper with a spatula. Do not grind or crush! Transfer the mixture into a large dry test tube. Heat the tube gently and evenly. The gas is collected over water as shown in the accompanying diagram. The test tube is fitted with a one-hole stopper and glass tubing. Rubber tubing is fitted to the glass tubing and extends to the jar of water inverted in a trough of water. As the oxygen is liberated, it bubbles through the water and pushes it out of the jar. Cover the jar with a wet glass plate and set it upright on the table. Collect as many bottles of oxygen as you can in this manner. When you are through,
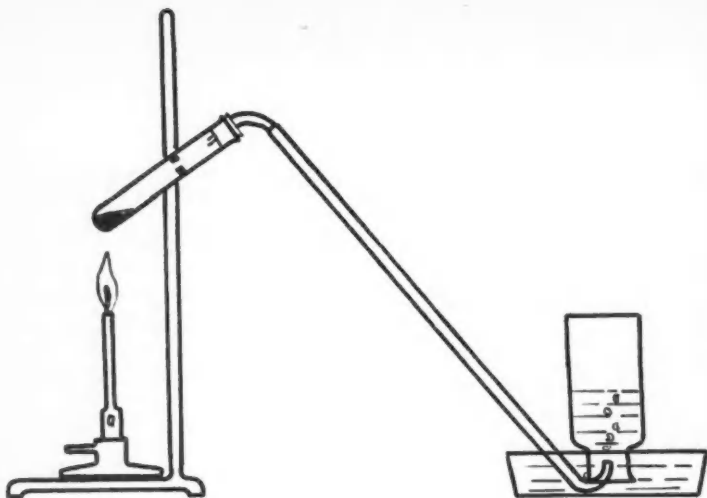
➤ PREPARATION *of oxygen.*

be sure to disconnect the rubber tubing before you remove the flame. This will prevent the water from being sucked back into the hot test tube.

Obtain a splinter of wood. Ignite it, then extinguish the flame until only a spark is still glowing. Immerse the glowing splinter into a bottle of oxygen. It will burst into flame and will continue to burn vigorously.

Ignite a tuft of steel wool by holding it in the alcohol lamp flame for a minute. Immerse the glowing wire into a bottle of oxygen. You will enjoy the sparkling display.

Charcoal will burn brilliantly in oxygen. Insert a glowing piece into

a bottle and observe for yourself.

There are many other items that you can burn in oxygen with spectacular results. Magnesium metal burns with a blinding white light. Sulfur burns with a large blue flame. Phosphorus burns with a bright yellow flame evolving large clouds of dense white smoke. In fact, any combustible substance will burn rapidly in pure oxygen.

You can devise other tricks and experiments with oxygen. Try placing moist iron filings in a bottle and note how quickly they rust. Or you can place a fly or beetle in oxygen and see how it reacts. You can even take a sniff yourself and see how you react!

ORGANIC CHEMISTRY

Hydrogen

HYDROGEN is the lightest of all the elements. One liter of it at 0° weighs only 0.08987 gram. Because of its extreme lightness, we can pour it upward from one vessel to another.

Although we can prepare hydrogen from water, it is much more convenient in the home laboratory to obtain it from chemical compounds. Acids contain hydrogen and they can be persuaded to part with it readily. For example, hydrochloric acid will part with its hydrogen in a reaction with zinc.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

Place a few pieces of zinc metal in a flask and add dilute hydrochloric acid. The action is vigorous and hydrogen is formed. Collect a test tube of hydrogen by holding the empty tube upside down over the mouth of the flask. As long as you hold the test tube upside down the hydrogen will not escape. Put the mouth of the test tube to a small flame placed some distance away from the generating flask. A sharp report is heard as the hydrogen combines explosively with the oxygen in the air. The result of this explosion, strangely enough, is water.

As you have just demonstrated, hydrogen mixed with air explodes when ignited. This means that you must use *extreme caution* when experimenting with it. Keep all flames a safe distance away from the vessel generating hydrogen.

Pure hydrogen, however, burns quietly. Because you cannot be sure
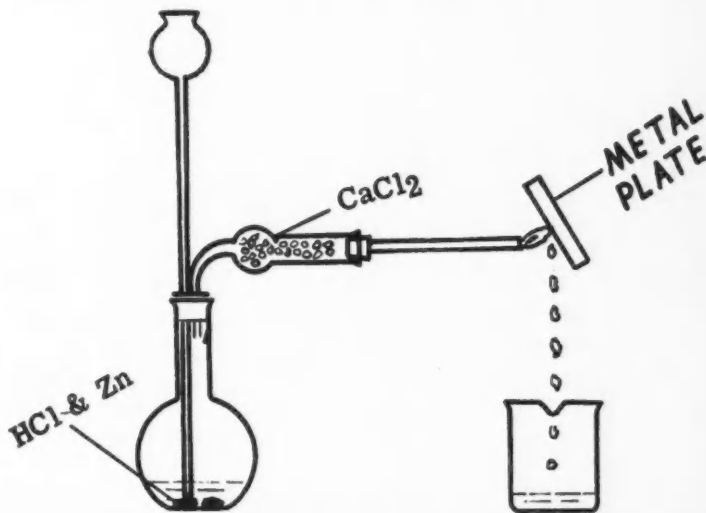
> SYNTHESIS of *water*

that hydrogen from a delivery tube of a generator is pure, the gas should *never* be ignited unless tests have shown that it is pure. Samples should be collected in test tubes, which are ignited away from the source. If the hydrogen burns quietly, you can be reasonably sure it is pure. For safety first, the hydrogen from the generator should *only* be ignited with a tube of burning hydrogen taken from the same generator.

Synthetic Water

➤ You CAN prepare water in the laboratory by the direct union of hydrogen and oxygen. Set up a hydrogen generator as shown in the accompanying diagram. Place zinc metal in the flask. The calcium chloride drying tube is inserted in the flask. Pour dilute hydrochloric acid through the thistle tube. Hydrogen is generated. *After* you have made certain that the hydrogen is pure, ignite it at the end of the delivery tube. As an added precaution, wrap a towel around the flask before igniting to prevent injury by acid or flying glass in the event of an explosion. Now hold a piece of metal or a beaker filled with cold water in the flame. Water will condense and run off the surface of the metal. So, if there is a drought, you can now manufacture your own water.

Hydrogen is an active reducing agent. It will reduce many metallic oxides to the pure metal.

Because of its light weight, hydrogen has great lifting power. Thus it is used in filling balloons and dirigibles, although it is now being replaced for this purpose by helium. The latter gas is also very light in weight and has the added advantage of being non-flammable.

You can demonstrate the lifting power of hydrogen by filling a toy balloon with it. Blow the balloon up several times in order to make it stretch easier. Then slip it over the mouth of a flask in which hydrogen is being generated. When the balloon is full, remove it and tie quickly to a long string. It will drift to the ceiling and stay there.

There are other methods of generating hydrogen. The more active metals, such as sodium, potassium and calcium, will generate it from water:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

It is formed from alkalies as well as acids by action with aluminum:

$$2Al + 6NaOH \rightarrow$$
$$2Na_3AlO_3 + 3H_2$$
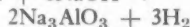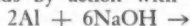
Commercially hydrogen is used for welding in the oxygen-hydrogen torch, in metallurgy by reducing oxides of metals, for filling dirigibles, to harden liquid fats (such as coconut and cottonseed oil), and in the synthesis of wood alcohol and ammonia.

Hydrogen Peroxide

➤ LET's become better acquainted with an old friend — the familiar "peroxide" from the medicine cabinet. We've used it on cuts and sores, we've gargled with it for sore throat, and (horrors!) perhaps we've even bleached our hair with it.

The ordinary drug store variety contains only 3% hydrogen peroxide. The remaining 97% is printed on the label as "inert ingredient": in other words, water. The chemist uses a 30% solution. During World War II, the Germans had prepared an 80%

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hydrogen peroxide which they reacted with sodium permanganate. The resultant mixture of steam and oxygen generated was used to drive the fuel pumps of the V-2 rockets. In this country, hydrogen peroxide of 95% purity has been produced.

The chief asset of hydrogen peroxide is its ability to oxidize readily. The higher concentrated variety is an exceedingly powerful oxidizing agent. It will ignite wooden splinters and fragments of cloth upon contact. Although it is fairly stable and will withstand shock, a slight trace of an organic compound will render it highly explosive. This does not seem at all similar to the medicine cabinet "peroxide," but it is the same compound, only more of it.

Preparation

Because it is inexpensive and easily obtainable, it is not practical to prepare hydrogen peroxide for home use. We include this instruction only for demonstration purposes.

Hydrogen peroxide is obtained by the inter-action of an acid with a peroxide. Barium peroxide is usually used. Place a small quantity of it in an evaporating dish and mix into a smooth paste with cold water. Then add a cold dilute solution of sulfuric or phosphoric acid and stir. When all action ceases, filter off the barium sulfate or phosphate to obtain hydrogen peroxide in the filtrate.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$
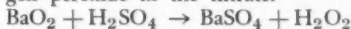
Add a little of your hydrogen peroxide to potassium permanganate solution. The red solution will turn colorless with effervescence.

Oxygen

Hydrogen peroxide decomposes into water and oxygen. The action is hastened by heat and light. This explains why it is always sold in amber colored bottles and should be kept in a cool place. Sometimes acetanilid is added to commercial solutions in order to retard decomposition.

Manganese dioxide will accelerate decomposition. To 5 cc. of hydrogen peroxide (3% variety) in a large test tube, add a small quantity of finely powdered manganese dioxide. The reaction will be moderately vigorous as oxygen is evolved. You can test for the latter by inserting a glowing splinter into the tube. The concentration of oxygen will cause the splinter to glow brighter or burst into flames.

Oxidation

Black to White. Hydrogen peroxide will oxidize black lead sulfide to white lead sulfate:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$
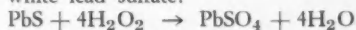
Prepare lead sulfide by mixing dilute solutions of lead nitrate and sodium sulfide. Then add hydrogen peroxide to transform black to white. This reaction is utilized in the restoration of old oil paintings which have darkened due to action of sulfides on the lead pigments in the paint.

White to Black. Hydrogen peroxide will oxidize white manganous hydroxide to black manganese dioxide:

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$$

Prepare manganous hydroxide by mixing dilute solutions of manganous sulfate and sodium hydroxide. Then add hydrogen peroxide to transform white to black.

Light Blue to Dark Blue. Mix together very dilute solutions of ferrous sulfate and potassium (or sodium) ferrocyanide to form a lovely light blue solution. The addition of hydrogen peroxide will immediately

change the color to dark blue. In this case the ferrous ion has been oxidized to ferric.

Colorless to Brown. Hydrogen peroxide will liberate iodine from iodides. Add a small quantity to a solution of potassium (or sodium) iodide. Immediately the colorless liquid turns brown as iodine is liberated and dissolves in the iodide solution.

Tests

There are many tests available to determine the presence of hydrogen peroxide. We will present only a few of the better known.

1. A pink solution of potassium permanganate is turned colorless by hydrogen peroxide.

2. Add a few drops of sulfuric acid to a solution of potassium dichromate. Upon the addition of hydrogen peroxide, a bright blue compound is formed which gradually turns to green. The actual composition of this blue compound is uncertain; it is probably perchromic acid.

3. Add a few drops of citric acid solution to a solution of ammonium molybdate. Hydrogen peroxide forms a yellow color with this mixture.

Uses

Industrially, hydrogen peroxide is used chiefly as a bleaching agent of such substances as hair, silk, straw, ivory, feathers, bone, gelatin, flour, etc.

Chemically, as illustrated above, it is used as an oxidizing agent.

Medically, it has long been used as a germicidal agent and antiseptic. We hesitate to betray an old friend, but we must report that recent bacteriological tests have questioned its efficiency in this respect.

Nitrogen

> IT MAY SURPRISE the average man to know that the greatest part of the air he breathes is not oxygen—but nitrogen. We have grown so familiar with the oxygen-carbon dioxide cycle, that we are prone to forget nitrogen which actually comprises 78% of the atmosphere.

We think of nitrogen in the air as a "useless" substance simply because it is inert. Actually, it is extremely important. Its presence dilutes the oxygen and thus slows down the process of oxidation. Without it, burning would be too rapid—decay and rust would run rampant—life would probably be much shorter.

Then there is the nitrogen cycle to consider. A special type of "nitrogen-fixing" bacteria which is present under the roots of leguminous plants (clover, peas, alfalfa, etc.) converts the free nitrogen of the air into nitrogen compounds which the plants can use. Finally, when living things die, decomposition sets in and eventually free nitrogen is restored again to the atmosphere. Thus the cycle repeats itself again and again, as it has since the dim beginning of life and probably will until the end of time. By this remarkable process of fixation and decomposition the ratio of nitrogen to oxygen remains constant.

Nitrogen can be obtained from the atmosphere, but it is a rather difficult and cumbersome process for the home laboratory. Commercially, the
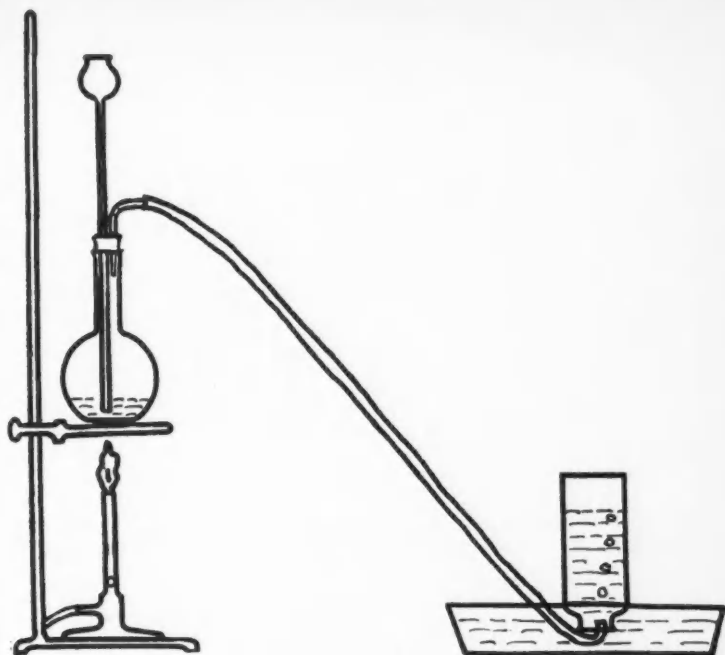
> COLLECTING *nitrogen over water.*

air is liquified and the nitrogen separated by fractional distillation.

In the laboratory, nitrogen can be obtained conveniently from its compounds. Ammonium nitrite, when heated, decomposes into pure nitrogen and water:

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$
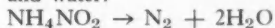
However, since ammonium nitrite is very unstable, there is some danger of explosion when it is heated. To avoid this danger, the ammonium nitrite is simultaneously prepared and decomposed in aqueous solution.

Mix together 5 grams of sodium nitrite with 4 grams of ammonium chloride in a large flask. Set up an apparatus designed to collect the gas over water, as shown in the accompanying diagram. Add about 30 cc. of water through the thistle tube and heat the flask gently. Allow the gas to bubble through the water in the trough a short time before collecting. When the bubbles form rapidly, place the rubber tube under the bottles in the trough and remove the flame from the flask. The nitrogen will displace the water in the inverted bottles. If the action in the flask should become too violent, pour in more cold water. If the bubbles form too slowly,

apply heat again *gently*. Collect several bottles of the gas. Cover with a glass plate and remove the bottles from the trough.

Now that you have gone to all the trouble of preparing nitrogen, about the only thing you can do with it is throw it away. As we pointed out before, nitrogen is rather inert and reluctant to combine with other elements at ordinary temperatures. It, of course, does not support combustion. Insert a burning splinter of wood into a jar of nitrogen. It will be extinguished immediately.

However, magnesium will continue to burn in nitrogen to form the *nitride*, Mg_3N_2. Ignite a small strip of the metal and insert in a jar of nitrogen.

Carefully remove the white residue, grind to a powder and add a few drops of water. Do you recognize the odor of ammonia?

———

That's about all we can do with nitrogen in the laboratory. Nothing spectacular about it,—but a mighty important element!

Oxides of Nitrogen

➤ To GIVE EXPRESSION to the private opinion of most chemistry students, the chief objection to the oxides of nitrogen is that there are too many of them. It is rather interesting to note that oxygen and nitrogen, which exist together in the elemental state under all atmospheric conditions, are capable of uniting with each other to form five different compounds. These compounds have somewhat unusual properties, and it will be worth our while to consider them in detail.

Nitrous Oxide, N_2O

➤ BETTER KNOWN as "laughing gas" or "sweet air," nitrous oxide is important as a local anesthetic—it is the "gas" the dentists use during extraction of teeth. When inhaled it produces somewhat intoxicating effects similar to those produced by an overindulgence in alcoholic beverages—so we have been told.

In order to study the properties of the gas, set up an apparatus whereby you can collect several bottles of it over water—preferably warm water

—similar to the method used to collect nitrogen. Use a flask as your generator fitted with a two-hole stopper, thistle tube, and delivery tube. Cover the bottom of the flask with pieces of mossy zinc. Pour 10 cc. of concentrated nitric acid in 100 cc. of water and transfer the mixture to the flask. If the reaction is too slow, heat until a steady stream of gas is given off and you are able to collect several bottles of it.

One striking property of nitrous oxide is its ability to support combustion. Glowing splinters, steel wool, sulfur, etc. burn almost as brightly in nitrous oxide as in oxygen. You can demonstrate this property readily in the home laboratory.

Nitrous oxide can also be obtained by heating ammonium nitrate; however, this method is rather dangerous and we do not recommend it for the home chemist. Being of a temperamental nature, ammonium nitrate is not to be trusted. If heated too strongly or unevenly, it may explode violently.

In 1921 a terrific explosion completely demolished a chemical plant in Germany devoted to the manufacture of ammonium nitrate. The factory disappeared entirely, leaving an enormous crater in the earth over fifty feet deep—grim evidence of the explosive potentiality of this compound! The Texas City disaster in 1947 was also due to an ammonium nitrate explosion.

Nitric Oxide, NO

➤ PLACE A FRESH quantity of zinc in your generator flask, and this time add to it a mixture of 5 cc. concentrated nitric acid and 20 cc. of water. The action will be more vigorous than before, and the flask will become filled with brown fumes. Wait until the brown fumes disappear, then collect a bottle or two of the gas, as before. Nitric oxide is colorless, but it readily reacts with oxygen to form the brown nitrogen dioxide, which explains why the brown fumes were observed at first in the flask. Remove the cover from one of your bottles of colorless nitric oxide; it will turn brown. Here is an opportunity for you to create a few "magic" experiments to fool your friends. You can show them a bottle of colorless "air" which will be colored brown merely by removing the stopper—or by blowing in the bottle, etc.

One important reaction of nitric oxide is with ferrous sulfate. Allow the gas to bubble through a solution of ferrous sulfate for a few minutes and notice the color change. This reaction is the basis of the familiar "brown-ring" test for nitrates. The nitrate solution is mixed with ferrous sulfate solution and concentrated sulfuric acid is added. The sulfuric acid

liberates nitric acid from the nitrate, and this in turn is reduced to nitric oxide:

$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$. The nitric oxide then forms the brown compound with ferrous sulfate ($FeNO.SO_4$) which identifies the nitrate.

Nitrogen Dioxide, NO_2 or Tetroxide, N_2O_4

➤ WE HAVE ALREADY prepared nitrogen dioxide by allowing nitric oxide to react with air. To prepare in quantity, add 5 cc. of concentrated nitric acid to zinc in a large flask. The action is quite vigorous and large clouds of red-brown gas are given off. (*Caution—poisonous! Do not inhale!*) Invert an empty flask above the generator to catch the gas. When filled with the brown fumes, stopper it.

Nitrogen dioxide is unique in that it changes color with the temperature. At low temperatures it is a yellow liquid; as the temperature rises it changes to a colorless gas, then pale yellow, light brown, and finally dark red-brown. The yellow liquid has the formula N_2O_4 and is a *polymer* of NO_2. At normal temperatures, both forms exist as a mixture.

You can observe the color changes of the gas by immersing the flask containing it in cold water. As the temperature drops, note the lighter color. By immersing the flask in warm water, the color darkens.

Nitrogen Trioxide, N_2O_3

➤ NITROGEN TRIOXIDE is formed temporarily when sulfuric acid is added to a nitrite, but under normal conditions decomposes rapidly into a mix-

ture of NO_2 and NO. Prepare a solution of sodium nitrite and add to it a small quantity of dilute sulfuric acid. Note the deep brown fumes of nitrogen dioxide.

If a mixture of the two gasses, NO_2 and NO, is cooled to around 3 degrees C., a blue liquid is formed which is probably N_2O_3. There has been some doubt as to the existence of nitrogen trioxide. Whether the blue liquid formed is actually a true compound, N_2O_3, or a mixture of two gases, NO_2 and NO, has not been fully determined.

Nitrogen Pentoxide, N_2O_5

➤ THE ANHYDRIDE of nitric acid, N_2O_5, is a white crystalline solid. It is not important and is difficult to obtain in a pure state. It can be produced by dehydrating nitric acid with phosphorus pentoxide.

We hope these experiments have proven of value in acquainting you more intimately with the family of oxides of nitrogen—an interesting and versatile group to say the least!

Chlorine

➤ LET US IMAGINE ourselves in the year 1774. And let us enter the laboratory of one Carl Wilhelm Scheele in Sweden. His laboratory is simple; he, of course has none of the modern equipment which we deem essential in our laboratories of today. He is intensely absorbed in his work. Upon closer examination we find he is experimenting with the mineral *pyrolusite,* which, he believes, contains a new substance. He now adds hydrochloric acid to a portion of pyrolusite and after a while he notices a greenish gas arising from the vessel. This commands his full attention, as he does not recall any vapor that is like this. He sniffs the gas and finds that it has a sharp suffocating odor. He is puzzled. What can this be? He is so handicapped by lack of knowledge! He does not know his acid is composed of hydrogen and chlorine. And he does not know the pyrolusite contains manganese dioxide. And he can never guess that the mineral is oxidizing the acid and thus setting the chlorine free. And, lastly, he does not

realize that he has discovered a new element—*chlorine!* In fact, it is considered a compound for over 36 years, when it is finally proven to be an element by none other than the illustrious Sir Humphry Davy.

Now back to the twentieth century where we can prepare the same chlorine from the same materials used by Scheele with the added advantages of purer compounds, better equipment, and more knowledge ... we hope.

Place two or three grams—no more —of manganese dioxide in the generator flask, (see diagram). Add hydrochloric acid through the thistle tube. Apply gentle heat and collect several bottles of the gas.

The excess chlorine is allowed to bubble through a solution of sodium hydroxide where it is absorbed. Precaution must be taken, as chlorine is very poisonous. Prepare only small quantities at a time in well ventilated surroundings. Do *not* inhale the gas! If you do accidentally inhale a large quantity of chlorine, breathing ammonia fumes will relieve irritation.

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Chlorine can also be obtained from common salt. Mix equal quantities of salt and manganese dioxide (about 1 gram of each) and place in the generator. Pour dilute sulfuric acid through the thistle tube. In this reaction, hydrochloric acid is formed by the action of sulfuric acid on the salt and is immediately oxidized by the manganese dioxide.

Chlorine is extremely active as can be demonstrated by the following reactions: Powdered antimony sifted into a jar of chlorine will burst into flame forming antimony trichloride, $SbCl_3$. Powdered iron, heated moderately, glows brilliantly to form ferric chloride, $FeCl_3$. A piece of filter paper moistened with turpentine ignites spontaneously in chlorine, emitting large clouds of soot. Colored papers, cloths, flowers, etc., when moistened with water are bleached white by chlorine. Actually, substances are not bleached by chlorine but by the hypochlorous acid which is formed by chlorine and water. And to be still more technical, it is not the hypochlorous acid but the atomic oxygen released by this compound that is really responsible for bleaching. Or, in a nutshell, the bleaching action of chlorine is due to oxygen ...!

Heated copper foil will burn in the gas resulting in a mist of cupric chloride, $CuCl_2$. Phosphorus burns feebly in chlorine to form the trichloride, PCl_3, or pentachloride, PCl_5, depending on the abundance of chlorine.(Use only a *very* small piece of phosphorus.) Melted sulfur unites to form sulfur monochloride, S_2Cl_2. Sodium unites with chlorine to form, obviously, sodium chloride.

To prepare synthetic salt, place a small, dry, freshly-cut piece of sodium
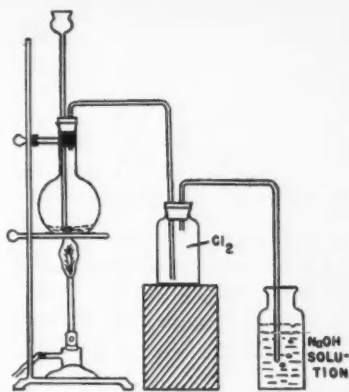
> PREPARATION *of chlorine*

in a jar of chlorine. It might be well to place the metal in a dry deflagration spoon; then lower into the jar. Allow to stand for about 30 minutes. Close examination will then reveal a white powder which is common table salt, although a rather expensive way to prepare it. If you are skeptical, dissolve the product in a large volume of water. Use a large container in the event all sodium has not reacted. Add silver nitrate and note the white precipitate indicative of the chloride ion. We do not recommend tasting as a method of proof.

Chlorine has many uses. In peacetimes it is used in the purification of water to save lives. In war times, it is used in poison gases to destroy lives. However, its latter use is being replaced by the atom bomb, which has been found to be much more effective. It is also used in the manufacture of dyes, drugs, explosives, disinfectants, germicidal preparations, in extracting gold from its ores and in reclaiming tin from "tin" cans.

Bromine

▶ THE NAME of bromine is derived from the Greek, meaning "a stench." And after you have performed this experiment you will no doubt agree that it has been appropriately named. Not only is the odor disagreeable, but also very irritating to the eyes and respiratory tract. The liquid itself is extremely caustic and if spilled on the skin will produce severe burns which are liable to become infected and are slow in healing. All in all, a rather unpleasant substance!

The chemical properties of bromine are similar to those of its older brother, chlorine, although not quite as energetic. Therefore, it is possible to displace bromine easily from its compounds with chlorine. The chlorine is prepared by adding 5 cc. of dilute hydrochloric acid to a small quantity of manganese dioxide in a test tube. Attach a stopper and delivery tube extending below the surface of a solution of potassium bromide in another container. Now heat the test tube slightly, allowing the gas to bubble through the bromide solution. Bro-

mine is immediately set free and imparts a deep orange color to the solution. This aqueous solution is *bromine water*. The chlorine passes into solution as potassium chloride.

Free bromine forms a yellow color with starch which you can easily demonstrate. Prepare a starch solution by adding a pinch of starch to 25 cc. water, boiling a few minutes, then thoroughly cooling. Add to a portion of bromine water.

Similar to chlorine, bromine water also bleaches. Prepare three solutions by boiling logwood, cochineal, and litmus in water. Add a little bromine water to each of the three colored solutions.

As chlorine displaces bromine, so bromine displaces iodine. Dissolve about ½ gram potassium iodide in 10 cc. of water and add bromine water. Notice the violet coloration as iodine is set free. Adding a few drops of this solution to starch solution will form the intense blue color, offering further proof of free iodine.

While bromine is fairly soluble in

KBr
solution

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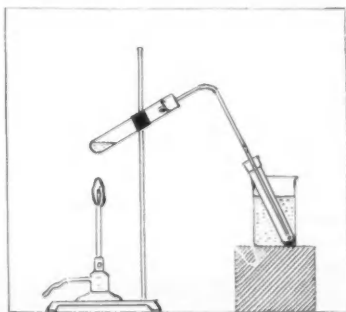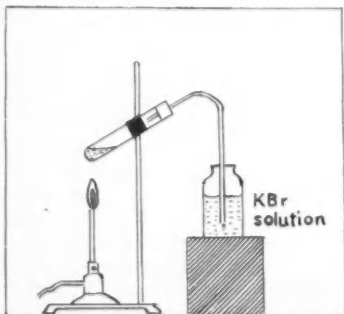
water, it is much more soluble in carbon disulfide, carbon tetrachloride, chloroform, ether, and similar organic solvents. Pour a few cc. of carbon tetrachloride in bromine water and shake thoroughly. After allowing to settle, note the deeper brown color in the layer of carbon tetrachloride. The same holds true for the iodine solution previously prepared. Here the carbon tetrachloride will be colored a lovely violet.

So far our attention has been focused on bromine water. Now we shall attempt to prepare the element itself. Again caution must be stressed. Many young lab enthusiasts tend to disregard warnings as they become more experienced and confident in experimenting. Confidence is an admirable trait, but it can also lead to carelessness!

Place a *small* quantity—about ¼ gram—of manganese dioxide and an equal quantity of potassium bromide in a test tube. Add a few cc. of dilute sulfuric acid. Attach a stopper and delivery tube leading to a test tube

immersed in a tumbler of cold water. Upon heating the first tube, deep clouds of brown vapor will be driven off and condense to a dark red liquid in the receiving tube.

Bromine combines directly with many metals, but less vigorously than chlorine. Throw a piece of magnesium ribbon in the bromine. It will dissolve quickly, forming a white powder which is, obviously, magnesium bromide. It finds use in medicine as a sedative.

Bromine first came to light in the year 1826, introduced by Antoine Jerome Balard who obtained it by adding chlorine to brines and distilling. It is interesting to note here that the great chemist Liebig almost discovered bromine. Earlier he had acquired an unknown substance, and upon testing not too thoroughly, he concluded that it was a compound of iodine. When the properties of bromine were made known by Balard, Liebig realized they were identical with his substance. His "compound of iodine" was actually bromine!

Iodine

▶ IODINE, the most beautiful and most gentle member of the halogen family, first saw the light of day in 1811 when it was isolated by Bernard Courtois from the mother liquor obtained from algae. Upon adding an excess of sulfuric acid to a concentrated portion of the liquor which he prepared by extracting the ashes of marine plants with water, Courtois was no doubt greatly surprised to see lovely clouds of deep violet vapor arising from the liquid. He found

that this vapor would condense to form dark lustrous crystals, and that these crystals would combine directly with certain metals, with phosphorus and with hydrogen. Later investigation by Gay-Lussac proved the substance to be a new element and it was christened *iodine,* from the Greek word meaning "like a violet."

To prepare iodine, mix together 2 grams potassium iodide and 3 grams manganese dioxide. Transfer the mixture to a small beaker and add 10 cc.
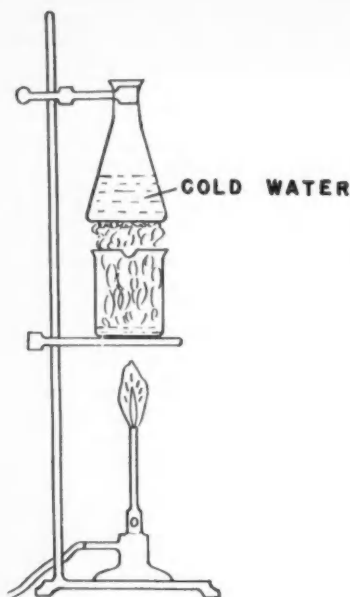
➤ Sᴜʙʟɪᴍᴀᴛɪᴏɴ *of iodine.*

of dilute sulfuric acid. Gentle heat will produce clouds of violet iodine vapor. Place a flask of cold water over the beaker, or cover the beaker partially with an evaporating dish. Crystals of iodine will form on the bottom of the flask or dish. The iodine passes from the gaseous state directly to the solid state. This process is known as *sublimation*. Scrape crystals off and dry them on blotting or filter paper.

To the average person iodine is known only in the form of the tincture, used as an antiseptic, which is a solution of iodine in alcohol. The medicine-cabinet variety usually contains 2% iodine. Although some people prefer the bright red of Mercurochrome to the brown of iodine, the latter's efficiency as an antiseptic cannot be denied.

Iodine will also dissolve in carbon tetrachloride or disulfide, forming a violet solution.

Another antiseptic compound of iodine is *iodoform*, CHI_3, a yellow powder with a characteristic "antiseptic" odor. Dissolve iodine crystals in potassium iodide solution until the liquid is dark brown in color. Add 5 cc. of this solution to an equal amount of alcohol. Now add sodium hydroxide solution in small proportions until the brown color disappears. Upon heating a few minutes and then cooling, a yellow precipitate of iodoform will separate out.

Another and perhaps better method of preparing iodoform is by dissolving 1 gram of potassium iodide in 20 cc. of water and adding 1 cc. of acetone. To this mixture add a dilute solution of sodium hypochlorite (you can use "Chlorox" from the grocery store). The yellow precipitate of iodoform is immediately formed.

The direct combination of iodine and phosphorus forms an exciting demonstration as these two elements celebate their union with a spontaneous display of fire. In a large evaporating dish, carefully place a *very small* piece of white phosphorus. Drop on the phosphorus a few small crystals of iodine. Keep your face a safe distance away. The mixture will suddenly burst into a brilliant flame, evolving large clouds of smoke. The result of this elaborate performance is a red compound, phosphorus tri-iodide, PI_3.

With red phosphorus, the action is much milder. If water be added to the mixture of red phosphorus and iodine, hydrogen iodide is formed:

$$2P + 3I_2 \rightarrow 2PI_3.$$
$$PI_3 + 3H_2O \rightarrow 3HI + H_3PO_3.$$
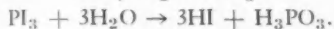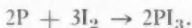
Speaking of hydrogen iodide, one would suppose it could be formed by the addition of sulfuric acid to an iodide (similar to hydrogen chloride). But such is not the case. Add a little sulfuric acid to a few crystals of potassium iodide in a dry test tube. You will notice the violet vapor of iodine and if you smell at the mouth of the tube you will no doubt recognize the delightful aroma of hydrogen sulfide. Now how did hydrogen sulfide get into the picture? Well, it appears that iodine was temporarily formed, but being much less stable than hydrogen chloride, it is therefore a more active reducing agent. And the nearest thing around for it to reduce is the sulfuric acid, which it promptly reduces to hydrogen sulfide:

$$H_2SO_4 + 8HI \rightarrow H_2S + 4H_2O + 4I_2$$
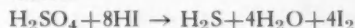
If you add a solution of sodium thiosulfate to a solution of iodine in potassium iodide, the brown color will entirely disappear. Hence this thiosulfate is an effective agent for removing iodine stains. You may use it to remove any brown stains you have acquired on your hands. Of course, if you have been a careful worker, there will be no stains to remove!

Fluorine

▶ THE ISOLATION of fluorine, the most active of all elements, required many long years of dangerous and painstaking research. Davy, Gay-Lussac, Thenard, the Knox brothers, Fremy and Gore were among the many noted chemists who tried unsuccessfully to free fluorine from its compounds. Louyet and Nickles both succumbed to the poisonous vapors of hydrogen fluoride and thus died martyers to science in their efforts to obtain the elusive fluorine. The long search finally ended when Moissan liberated the element in 1886, after many unsuccessful attempts and much suffering from inhaling hydrofluoric acid vapors. His method consisted of the electrolysis of dry potassium bifluoride dissolved in anhydrous hydrofluoric acid cooled to a temperature of 23°. He used platinum-iridium electrodes in a platinum U-tube covered with fluospar caps.

Assuming that the average home lab is not equipped with the elaborate apparatus necessary for the preparation of fluorine, we must confine our interests to the properties of the compounds of fluorine. All fluorides are poisonous and therefore must be handled carefully. Hydrofluoric acid is extremely caustic causing painful sores if spilled on the skin; its vapor is irritating and must not be inhaled.

Etching Glass

Although hydrofluoric acid is a relatively weak acid and reacts slowly upon metals, it is unique in that it reacts readily with silica and silicates:

$$CaSiO_3 + 6HF \rightarrow$$
$$SiF_4 + CaF_2 + 3H_2O.$$
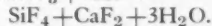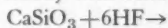
Hence it attacks glass, porcelain, clay-

wares, etc. This property is utilized in the etching and frosting of glass articles.

Cover the article to be etched with a thin coating of wax. The design or lettering is then made by cutting through the wax with a sharp instrument. The hydrofluoric acid vapors will attack that portion of the glass exposed producing a rough surface. Burettes and other glassware are graduated in this manner.

To prepare the hydrofluoric acid, mix 1 gram of calcium fluoride with enough sulfuric acid to form a thin paste. The mixture must be placed in a lead dish. Or if you have a few platinum or iridium dishes, they may be used instead. Now place the wax-coated glass over the dish and allow to stand overnight. The action can be hastened by gently warming the dish, but care must be taken not to melt the wax and thus spoil the design. After sufficient exposure to the acid vapors, the wax is removed by melting, leaving the etched outline of the design on the glass.

Fluosilicates

When concentrated sulfuric acid is added to a small quantity of a mixture of silica and calcium fluoride, silicon tetrafluoride, a gas, is given off. This gas dissolves readily in water, forming silicic acid and fluosilicic acid. The former can be re-moved by precipitation, leaving the latter in solution:

$$3SiF_4 + 4H_2O \rightarrow$$
$$H_4SiO_4 \downarrow + 2H_2SiF_6$$
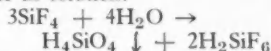
Potassium fluosilicate (or silico-fluoride) is one of the few salts of this metal which is insoluble in water. For this reason, fluosilicic acid is used in analysis. If potassium chloride solution be added to the fluosilicic acid, a translucent and gelatinous precipitate is formed which will be increased by the addition of alcohol.

Organic Fluoro Compounds

Recently many new fluoro compounds have been prepared with the possibilities of many more yet to be investigated.

One of the most useful of these compounds is dichlorodifluoromethane (CCl_2F_2), commonly known as "freon" which is widely used as a refrigerant. It is ideal for this purpose and is rapidly replacing sulfur dioxide, ammonia, and methyl chloride in both household and commercial refrigeration. It is stable, non-poisonous, non-flammable, non-corrosive and has very little odor. It is formed by the action of antimony trifluoride on carbon tetrachloride, using antimony pentachloride as a catalyst. The net result of this reaction is the replacement of two chlorine atoms in carbon tetrachloride by fluorine:

$$3CCl_4 + 2SbF_3 \rightarrow 3CCl_2F_2 + 2SbCl_3$$
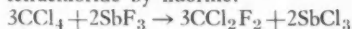
Sulfur

▶ THROUGH its evil-smelling compounds, sulfur has gained a rather bad reputation. Although many sulfur compounds do yield an offensive odor, the element itself is odorless and tasteless.

Despite the bad smells, sulfur is an extremely useful substance. One of its compounds, sulfuric acid, is the most useful chemical substance ever manufactured. About 10,000,000 tons of it are consumed each year in the

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United States alone. Another important use of sulfur is in the vulcanization of rubber. It is also used in fungicides, gunpowder, fumigants, and in the manufacture of hundreds of important compounds.

Sulfur has been known since the dawn of history. It was used as a fumigant and in medicine as early as 1000 B.C. It is the "brimstone" of the Bible.

Allotropic Forms

Rhombic Crystals. Sulfur exists in two allotropic crystalline forms, the most stable of which is the rhombic.

Dissolve about 0.5 gram of sulfur in 4 cc. of carbon disulfide. If necessary, filter the solution. Pour the clear filtrate in a watch glass and allow to evaporate spontaneously. Do not heat. Examine carefully the crystals that remain. Note the formation—like two pyramids base to base.

Monoclinic Crystals. Heat gently a small amount of sulfur in a dry test tube. Heat until the sulfur just melts to a thin, light amber colored fluid. Be careful not to overheat. Pour the liquid into a dry filter paper in a funnel. As soon as a portion of the liquid begins to solidify, quickly pour off the excess liquid. Open the filter paper and examine the crystals with a magnifying glass. Note this time they are long, transparent and rectangular shaped.

Amorphous (Plastic) Sulfur. Heat again about one gram of sulfur in a dry test tube. It will melt to the amber-colored fluid. Continue heating. The liquid will turn dark orange and finally into a black mass. Continue to heat until the mass is again fluid and just begins to boil. Then pour quickly into a beaker of cold water. Do this carefully, as the vapor may ignite. Examine the mass in the beaker. You will note that it is plastic and elastic, similar to rubber. However, this condition is not permanent. Upon standing it becomes brittle and returns to the rhombic form. The strange part of it is that in this condition, sulfur is not soluble in carbon disulfide. Also, a minute trace of sulfuric acid must be present in the sulfur in order for it to be plastic. Absolutely pure sulfur does not form the plastic allotrophy.

Colloidal Sulfur (Milk of Sulfur). Colloidal sulfur consists of small rhombic crystals. It is formed readily by adding a few drops of hydrochloric acid to a solution of sodium thiosulfate. When the acid is first added, nothing appears to happen. Then, after a few seconds, a white color is suddenly formed which rapidly develops into a yellow precipitate of colloidal sulfur.

Sulfides

Sulfur combines with most of the metals and many of the non-metals to form sulfides. Here are a few of them:

Iron Sulfide. Heat equal portions of powdered sulfur and iron filings in a metal crucible or lid. Heat until the sulfur ceases to burn. The remaining mass is ferrous sulfide.

Hydrogen Sulfide. Break up a few lumps of the ferrous sulfide just prepared. Place in a test tube and add dilute hydrochloric acid. You will soon recognize the rotten-egg odor of hydrogen sulfide.

Zinc Sulfide. The formation of zinc sulfide is accompanied by a pyrotechnical display. Mix together two parts of powdered zinc with one part

of sulfur. Use small quantities. Place the mixture in a neat pile in a large metal pan. It can now be ignited by touching it with a hot glass rod. Keep your distance! Sometimes, the sulfur alone is ignited and burns quietly with a blue flame. Even so, be patient and still keep your distance. The mixture will suddenly, without warning, burst into a brilliant and violent green flame accompanied by large clouds of white smoke. To avoid all danger of fire, perform this experiment outside, or on the concrete floor of the basement.

Mercuric Sulfide. It is not even necessary to apply heat to obtain mercuric sulfide. Simply grind together a small globule of mercury with a little sulfur in a mortar. A black amorphorus powder is obtained. However, if the two elements are heated together, the red variety of mercuric sulfide (vermilion) is obtained.

Oxides

As you probably have observed by now, sulfur burns in air with a blue flame forming *sulfur dioxide.* SO_2. And as you have probably noticed by now, the latter has a pungent, irritating odor. Sulfur dioxide is a very interesting and useful compound and we will investigate its properties more thoroughly below.

When sulfur dioxide is interacted with oxygen, by means of a suitable catalyst, *sulfur trioxide.* SO_3, is obtained. It is a white solid which dissolves in water to form sulfuric acid.

Other oxides of sulfur have been isolated. If you are interested, they are the *monoxide,* SO, a gas formed by the action of an electric discharge on sulfur dioxide and sulfur vapor at low pressure; the *sesquioxide,* S_2O_3, a blue-green solid; and the *heptoxide,* S_2O_7, a thick liquid.

Sulfur Dioxide

It Is Prepared Easily

In the home lab, sulfur dioxide is most conveniently prepared by the action of dilute acids on sodium bisulfite. In a large flask, place 2 or 3 grams of sodium bisulfite and cover the solid with about $\frac{1}{4}$ inch of water. Fit a 2-hole stopper to the flask containing a thistle tube and delivery tube. Be sure the thistle tube extends beneath the surface of the liquid in the flask. When you are ready to generate sulfur dioxide, simply pour dilute hydrochloric acid, in small quantities, through the thistle tube.

It Will Dissolve In Water

Arrange your delivery tube from the generator so that the gas will bubble through water in a test tube. It will dissolve readily forming a solution of sulfurous acid, H_2SO_3. The acidic properties can be identified with litmus paper.

It Will De-Colorize

Bubble the gas through a dilute solution of potassium permanganate. As each bubble enters the solution, the violet color fades slightly until the solution is entirely colorless.

It Can Be Liquefied

Sulfur can be liquefied very easily at atmospheric pressure with salt and ice mixture. Insert a U-tube in a con-

Oxidation
SO_2 → ← H_2S
H_2O

Reduction
SO_2 → CuO

Generator
HCl
→ SO_2
$NaHSO_3$

Liquefication
SO_2 →
ICE AND SALT

Bleaching
SO_2
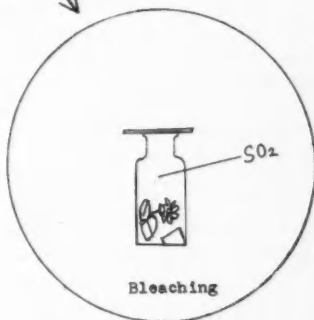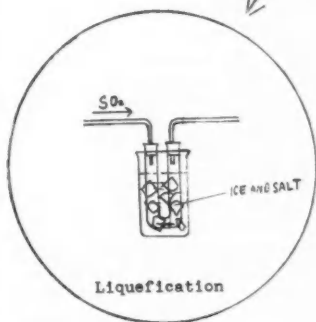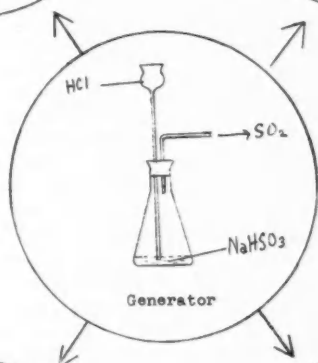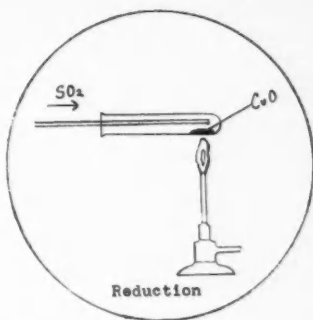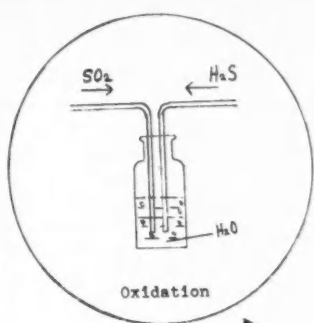
▶ VERSATILE *sulfur dioxide plays many roles in the home laboratory theater.*

tainer filled with crushed ice and salt. Attach the delivery tube of your SO_2 generator to the U-tube and allow the gas to pass through. Soon you will note a colorless liquid forming in the bottom of the U-tube. This is liquid sulfur dioxide. Remove the tube from the ice and you will observe that the liquid gradually boils away.

It Will Bleach

Fill a large jar with sulfur dioxide. Moisten a few bits of colored paper, cloth, flowers, leaves, etc. and place in the jar. Cover with a glass plate and let stand for a while. Sulfur dioxide will bleach many items (but not everything), especially silk, wool, straw and flowers, although in most cases the bleaching is not permanent.

It Will Preserve

Place half of a freshly cut red apple in a jar of sulfur dioxide. Take notice that the brown discoloration that usually takes place in air does not occur in an atmosphere of sulfur dioxide, although the red skin will be bleached. Sulfur dioxide has been used as a preservative in many foods; however, its use in this category has been questioned and is still open to argument.

Incidentally, if you want to restore the red color to your apple, rub the skin with hydrogen peroxide. But don't eat it!

It Will Oxidize

Sulfur dioxide is not generally known as an oxidizing agent, but it will oxidize hydrogen sulfide, producing free sulfur:

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S.$$
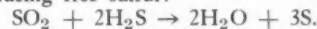
You can demonstrate this reaction by bubbling sulfur dioxide through an aqueous solution of hydrogen sulfide. Or, if you wish, bubble both sulfur dioxide and hydrogen sulfide through water simultaneously. The hydrogen sulfide is prepared by adding dilute hydrochloric acid to iron sulfide.

It Will Reduce

Sulfur dioxide is better known as an active reducing agent. For example, it will reduce the oxides of many metals. Place a small quantity of cupric oxide in a dry test tube. With the tube in a horizontal position, apply heat and allow sulfur dioxide to flow over the heated powder for a few minutes. Then remove and examine closely. Can you find any trace of metallic copper?

And It Will Affect You

Are your eyes smarting? Nose running? Throat burning? If so, you've had enough for a while. So let's get some fresh air and call it a day.

Sulfuric Acid

➤ SULFURIC ACID—"King of Chemicals"—is perhaps the most useful compound ever manufactured. It can be used as an acid, catalyst, dehydrating agent, oxidizing agent, electrolyte and solvent.

Sulfuric acid is not easily manufactured. The dioxide of sulfur, SO_2, is a complacent compound and thus is reluctant to accept another atom of oxygen to form the trioxide, SO_3, which is the anhydride of sulfuric acid. To bring about this transformation, the chemist must use rather persuasive methods, such as employing a catalyst. Sulfur dioxide and air are

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heated and passed over the catalyst, which usually consists of mixtures containing vanadium pentoxide. Sulfur trioxide is formed, $2SO_2 + O_2 \rightarrow 2SO_3$, from which acid is produced.

Another method utilizes the action of the oxides of nitrogen on sulfur dioxide. This is the method which can be demonstrated in the laboratory. Commercially, it is known as the "Lead Chamber" process.

First, secure a flask to be used as the "Lead Chamber," or reaction flask, and fit it with a three-hole rubber stopper. Now we must supply a source of sulfur dioxide. This is most conviently prepared in the laboratory by the action of HCl on sodium bisulfite. Place four grams of the latter in a flask and just cover it with water. Fit the flask with a two-hole stopper, thistle tube and delivery tube. The end of the thistle tube should be just under the surface of the water in the flask. The delivery tube should lead to the reaction flask.

Next we must supply a source of nitrogen dioxide, which can be obtained readily by heating the nitrate of a heavy metal such as copper or lead. Place three grams of copper nitrate in a dry test tube. Clamp in an inclined position and fit with a stopper and delivery tube leading to the reaction flask.

An outlet tube is placed in the third hole of the stopper in the reaction flask. This can be connected to a rubber tube leading the offensive gases away, or the gases may be absorbed in water, after first passing through an empty bottle as a "trap." This rather elaborate apparatus can be set up in several ways.

Heat the copper nitrate until the reaction flask is filled with brown fumes. Then pour hydrochloric acid through the thistle tube of the SO_2 generator. Allow the two gases to flow into the reaction flask, keeping the NO_2 slightly in excess. After a while, thin white crystals will form in the flask, and will dissolve in any water that may have condensed, forming numerous droplets of acid.

After you have choked considerably from the fumes, discontinue the reaction and disconnect the apparatus. Pour a little water on the crystals that have formed. Notice the sizzling sound. Sulfur trioxide reacts with the water to form sulfuric acid: $SO_3 + H_2O \rightarrow H_2SO_4$.

Pour a portion of the acid into a solution of barium chloride. A heavy white precipitate indicates the presence of the sulfate radical. Test the strength of the acid by adding a small piece of zinc; it should react, liberating hydrogen.

Of course, this method is not practical, being designed solely for demonstration purposes. In the commercial Lead Chamber process, the sulfur dioxide is produced by burning sulfur or iron pyrites. The oxides of nitrogen are produced by the catalytic oxidation of ammonia. The two gases, along with air, are led into the Lead Chamber where steam is introduced.

Reaction occurs, producing *nitrosyl* sulfuric acid: $2SO_2 + NO + NO_2 + O_2 + H_2O \rightarrow 2NOHSO_4$, which in turn reacts with more water forming sulfuric acid: $2NOHSO_4 + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$. You will note that the oxides of nitrogen are again produced by the second reaction. These are collected and used over again.

The Home Lab as a Hobby

➤ As a suitable location for the home lab, a corner of the cellar is probably best, preferably near a window. Running water and gas are convenient, but not absolutely necessary.

Find or construct a suitable work bench. The basic requirements are that it be sturdy, of convenient height, spacious, and covered with a suitable washable material, such as linoleum, or a slab of marble. If you have running water available, you would allow space for a sink at one end of the bench. If not, keep a large pitcher of water handy and a bucket or large jar for waste. Or, if you wish, you can construct a siphon arrangement. Shelves can be built on the wall next to or back of the table.

Now you are ready to stock your lab. It is rather difficult to list what should be purchased at first. Perhaps the best thing would be to purchase one of the many chemistry sets on the market today — for about five or ten dollars. This will provide you with a varied selection of the more common chemicals. From time to time purchase more chemicals and apparatus and in this way gradually enlarge your laboratory without too much financial trouble. Start from the bottom; you cannot expect to obtain a well-equipped laboratory overnight.

At first, perform simple experiments. Later purchase a good textbook and perform some of the experiments described in it. Experiments appear periodically in many scientific journals, such as those in this series, designed primarily for the home lab.

As your laboratory progresses, so you will progress to more difficult and fascinating experiments. Soon you will find that you will be performing experiments of your own — following miniature projects of your own. Here you will experience a new kind of pleasure, a creative pleasure, the joy of discovering things for yourself!

Some may question the danger of a home lab. A home lab is no more dangerous than any other hobby, if you simply abide by one principle: *Use common sense!* Naturally, you will handle corrosive liquids and dangerous poisons carefully. You will provide yourself with adequate protection when experimenting with explosive mixtures. And of course you will not expose flammable liquids to open flames. Do not mix everything together, "to see what will happen." Think out your experiments before performing them. Investigate the subject and deduce what will happen — then proceed with proper preparations.

Neatness is an important factor. Nothing is more discouraging than an untidy, unkempt lab. Keep all of your chemicals properly and neatly labeled and arranged on the shelves in systematic order so that you may locate them quickly. Wash all dishes after each experiment and keep all apparatus clean. Dirty containers can spoil many experiments.

Finally, go to it and have fun! The home lab enthusiast of today may become the scientist of tomorrow!

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General Instructions

The experiments described herein have been especially adapted for performance in a home laboratory. Extremely complex reactions which involve costly and intricate equipment have been avoided. Most experiments can be done with ordinary equipment and reagents which are obtainable from laboratory supply houses.

Only small scale operations are used. If it is desired to prepare larger quantities of any substance, simply increase all quantities of reagents used proportionally. However, we suggest that you get into the habit of experimenting with small quantities for convenience, safety, and economy.

Many reagents deteriorate with age. For best results, use pure fresh reagents in all reactions. Although quality is not specified, it is a good idea to use C.P. reagents if possible. In many cases exact quantities are not specified. This is because an exact strength is not required. When a "solution" of a compound is mentioned, we suggest you use an approximate 10% solution, or one gram of the compound in 10 cc. of water. A "small quantity" of a solid substance usually means $\frac{1}{4}$ to $\frac{1}{2}$ gram, or a "pinch". However, when specific quantities are stated, it is suggested that you adhere to them for best results.

$\bigstar$

Words of Caution

In many experiments you are advised to take special care or to proceed cautiously. We cannot stress too strongly the necessity for abiding by these words of warning. They are not included simply to take up space, but are issued for your personal safety. Sometimes you may feel that the warnings are exaggerated and you may be inclined to ignore them. This is a dangerous mistake! *Never disregard warnings!*

The experiments herein can be performed with complete safety if ordinary common sense is exercised and all warnings heeded. You will be handling highly corrosive acids and highly flammable compounds. Treat them with respect. Inhale vapors cautiously at all times and provide adequate ventilation. Protect your eyes at all times! Remember, eyesight is priceless and once gone can never be replaced!

Work in clean surroundings, for a cluttered and sloppy workbench will discourage anyone. Clean all apparatus after experimenting and be sure to replace the caps on all reagents promptly to prevent deterioration and evaporation.

Work carefully, take your time, and enjoy yourself!